

AN ABSTRACT OF THE THESIS OF

Nathaniel J. Coussens for the degree of Honors Baccalaureate of Science in Chemical Engineering presented on May 29, 2009. Title: Lanthanum Sulfide Thin Film Deposition via Chemical Nanocluster Deposition.

Abstract approved:

Chih-hung Chang

Lanthanum sulfide film was deposited on silicon dioxide substrate by pumping aqueous $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ solutions into a T-mixer. After mixing, residence time was manipulated to adjust lanthanum sulfide deposition rate. Lanthanum sulfide films were created on silicon dioxide substrate at room temperature, 60 °C, and at 100 °C.

Lanthanum sulfide films were analyzed for particle size and crystalline structure using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis. The film material bandgap was characterized to be about 3.5 eV from UV-Vis analysis. TEM results indicate that the film grown has both polycrystalline and amorphous regions. Particle size was determined to range from ~1-50 nm after 20 seconds of deposition. The growth profile for lanthanum sulfide deposition follows a linear trend at room temperature.

Key Words: lanthanum sulfide, nanocluster, thin film deposition

Corresponding e-mail address: coussenn@onid.orst.edu

©Copyright by Nathaniel J. Coussens

May 29, 2009

All Rights Reserved

Lanthanum Sulfide Thin Film Deposition
via Chemical Nanocluster Deposition

By

Nathaniel J. Coussens

A PROJECT

submitted to

Oregon State University

University Honors College

in partial fulfillment of
the requirements for the
degree of

Honors Baccalaureate of Science in Chemical Engineering (Honors Scholar)

Presented: May 29, 2009
Commencement: June 2009

Honors Baccalaureate of Science in Chemical Engineering thesis of Nathaniel J. Coussens
presented on May 29, 2009.

APPROVED:

Mentor, representing Chemical Engineering

Committee Member, representing Chemical Engineering

Committee Member, representing Chemical Engineering

Chair, Department of Chemical Engineering

Dean, University Honors College

I understand that my project will become part of the permanent collection of Oregon State University, University Honors College. My signature below authorizes release of my project to any reader upon request.

Nathaniel J. Coussens, Author

TABLE OF CONTENTS

| | |
|--|-----------|
| 1. INTRODUCTION | 8 |
| 1.1 OVERVIEW OF COMMON THIN FILM DEPOSITION TECHNIQUES AND THEORY | 9 |
| 1.2 THIN FILM DEPOSITION TECHNIQUES | 9 |
| 1.2.1 Atomic Layer Epitaxy..... | 9 |
| 1.2.2 Chemical Bath Deposition | 2 |
| 1.2.3 Successive Ionic Layer Adsorption and Reaction (SILAR) | 2 |
| 1.2.4 Spray Pyrolysis..... | 3 |
| 1.2.5 Nanocluster Deposition..... | 3 |
| 1.2.5.1 Benefits and Disadvantages to Nanocluster Deposition | 4 |
| 1.3 THEORY OF NANOCUSTER DEPOSITION PROCESS | 5 |
| 1.3.1 Solubility Product | 5 |
| 1.3.2 Optimization Parameters | 6 |
| 1.3.2.1 Temperature | 6 |
| 1.3.2.2 Reactor Length | 6 |
| 1.3.2.3 Spin Rate | 7 |
| 1.3.2.4 Reactant Concentrations..... | 7 |
| 1.3.2.5 Film Thickness | 8 |
| 2. EXPERIMENTAL PROCEDURE | 9 |
| 3. RESULTS..... | 11 |
| 3.1 QUALITATIVE ANALYSIS OF SEM RESULTS..... | 11 |
| 3.2 PROFILOMETER READINGS ON FILM THICKNESS | 12 |
| 3.2.1 Profilometer Data for Different Techniques..... | 15 |
| 3.3 ULTRAVIOLET-VISIBLE SPECTROMETRY DATA..... | 16 |
| 3.4 ANALYSIS OF TEM RESULTS | 18 |
| 3.5 EDX DATA | 20 |
| 4. CONCLUSIONS..... | 21 |
| APPENDIX A..... | 22 |
| APPENDIX B..... | 24 |
| BIBLIOGRAPHY | 26 |

LIST OF FIGURES

| | |
|--|----|
| Figure 1: Nanocluster Deposition Process..... | 5 |
| Figure 2: T-mixer Setup for nanocluster deposition experiment..... | 9 |
| Figure 3: SEM Images of Lanthanum Sulfide. | 12 |
| Figure 4: Film Growth Rate versus Time for films grown in Table 2 | 15 |
| Figure 5: Band-gap Determination from UV-Vis..... | 17 |
| Figure 6: TEM image of lanthanum sulfide material. | 19 |
| Figure 7: TEM image of lanthanum sulfide particles.. | 19 |
| Figure 8: EDX Data.. | 20 |

LIST OF TABLES

| | |
|---|----|
| Table 1: Lanthanum Sulfide Film Thickness Data taken by Profilometer... | 13 |
| Table 2: “Optimal Condition” Lanthanum Sulfide Film Thickness Data | 14 |
| Table 3: UV-Vis Bandgaps.. | 16 |

1. INTRODUCTION

1.1 Overview of Common Thin Film Deposition Techniques

The present thesis focuses on the thin film deposition of lanthanum sulfide. La_2S_3 has several applications, including use in phosphors and use in semiconductors.^{1,2,3}

Several techniques have been used in the creation of La_2S_3 films, including: atomic layer epitaxy, spray pyrolysis, and chemical vapor deposition.^{1,2,3} Each of these methods will only briefly be discussed to show what differentiates the nanocluster method from other thin film deposition methods. The deposition method used in this thesis is distinctly different from all commonly practiced methods described, but resembles most closely spray pyrolysis.

1.2 Thin Film Deposition Techniques

1.2.1 Atomic Layer Epitaxy

Atomic Layer Epitaxy, or ALE, is one technique which is known to produce highly uniform films. High uniformity is achieved through the ability to control deposition within a fraction of a monolayer.⁴ ALE occurs in a four-step process. First, one of the

two reactant gases is applied to the substrate. Then, this reactant gas is removed. Then, the second reactant gas is introduced. Finally, this reactant gas is removed. This four-step process should effectively produce one monolayer of thin film on the substrate. The high uniformity of this method is achieved with the drawback of high costs resulting from high operating temperatures.⁴

1.2.2 Chemical Bath Deposition

Chemical bath deposition is a commonly used solution based method for thin film deposition. In this method, the substrate is immersed for a period of time to grow a thin film. A process which implements chemical bath deposition is the deposition of cadmium sulfide in the production of CdInSe₂/CdS thin film solar cells. Here, chemical bath deposition of CdS is achieved by applying the substrate to a bath of cadmium chloride, triethanolamine, and thiourea.⁵

1.2.3 Successive Ionic Layer Adsorption and Reaction (SILAR)

Successive Ionic Layer Adsorption and Reaction, or SILAR, has been used to achieve uniformity similar to that encountered in Atomic Layer Epitaxy. For SILAR deposition, a four-step process is used. First, a solution containing negatively charged anion precursors is applied to the substrate. Next, the substrate is purged with deionized

water. Then, a solution containing positively charged precursors is applied to the substrate. Finally the substrate is again purged.⁶ This process, in turn, should result in a monolayer of film deposition in the same way that Atomic Layer Epitaxy does. The key difference between the two processes is that ALE uses gas reactants whereas SILAR uses aqueous reactants.

1.2.4 Spray Pyrolysis

The deposition method most similar to the technique used in this paper is spray pyrolysis. In the spray pyrolysis of lanthanum sulfide conducted by Bagde et al, a slurry of lanthanum sulfide was deposited on a heated glass substrate using an atomizer.³ The lowest deposition temperature highlighted in the paper was at 150 °C, with optimum conditions found to occur at 275 °C.³ By reducing the amount of required heat, the process would become less expensive.

1.2.5 Nanocluster Deposition

The process used in this paper is focused on directly depositing lanthanum sulfide in a manner similar to the spray pyrolysis technique. This nanocluster deposition process is solution-based, whereas other nanocluster deposition processes in literature are vapor-based (such as ZnO nanocluster deposition by Antony et al).⁹ Initially, the substrate is prepared in such a way that adsorption of the desired anion is favorable (in the paper,

hydroxide ions are adsorbed on the surface for this purpose). The deposited lanthanum sulfide particle size was controlled by depositing a solution containing partially reacted solution seconds after the anionic and cationic components are combined. By pre-reacting lanthanum and sulfide source materials in this controlled manner, the film thickness could be controlled. Further, the deposition took place on a spinner to ensure a continual supply of fresh solution, and temperature was manipulated to optimize growth. Further detail for the optimization process will be discussed in section 1.3.2. It should be emphasized that nanocluster deposition differs from a spray pyrolysis-based method. Nanocluster deposition facilitates the pre-formation of products before deposition on the substrate, whereas spray pyrolysis forms product on the substrate. In spray pyrolysis, the temperature of the substrate itself is used for the formation of product directly on the substrate surface.

1.2.5.1 Benefits and Disadvantages to Nanocluster Deposition

There are some disadvantages to solution-based nanocluster deposition. The currently proposed method has the disadvantage of uniformity issues. However, the biggest benefit to nanocluster deposition, and solution-based thin film deposition in general, is lower process costs. Nanocluster deposition can take place at lower temperatures, and the film can be created without the use of vacuum conditions. Nanocluster deposition is

described in detail in the experimental procedure. An overview of the method is highlighted in the figure below.

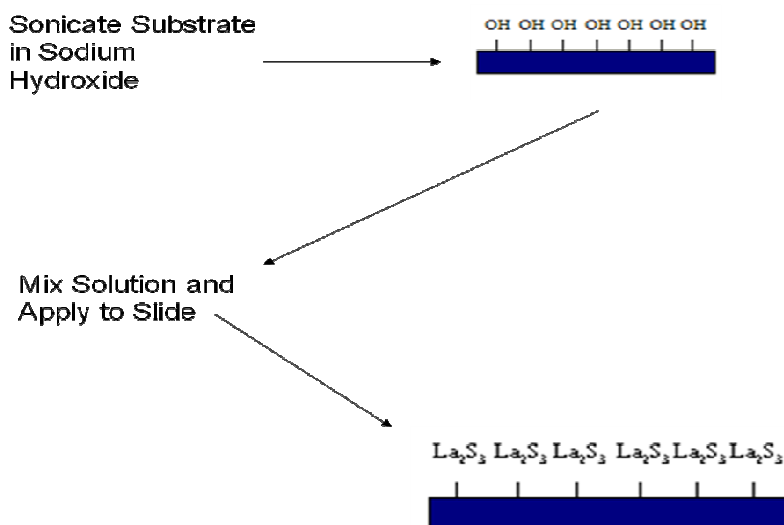


Figure 1: Nanocluster Deposition Process.

1.3 Theory of Nanocluster Deposition Process

1.3.1 Solubility Product

In the case of lanthanum sulfide, the solubility product is suspected to be low. While no literature value for the solubility product could be found, a distinct white precipitate will form when combining very low concentrations of lanthanum chloride and sodium sulfide together. For this reason, a considerable amount of the product will precipitate out before reaching the substrate, leading to a considerable loss in substrate film growth rate.

1.3.2 Optimization Parameters

1.3.2.1 Temperature

Typically for thin film deposition, colder films will deposit with smaller particles (p. 12-13).⁷ This leads to a film deposition mechanism referred to as homogeneous nucleation (p. 12-13).⁷ Therefore, temperature is one important aspect to film deposition which needs to be explored.

1.3.2.2 Reactor Length

Presently, reactant lanthanum and sulfide ions are directly mixed together to form a product. This reaction is expected to go towards completion as a function of length. Determining the exact reaction mechanism for the production of lanthanum sulfide is not a subject of this paper. However, an intuitive understanding of how particle formation varies with reactor length is important. As the anionic and cationic molecules react, lanthanum sulfide will form. Lanthanum sulfide molecules will then aggregate together to form nanoclusters. The reactor length will need to be optimized so that the extent of reaction is small enough that the particles deposited remain on the nano-scale, which should lead to better film uniformity. However, the reactor length will

need to be kept large enough that the film grows in what would be considered a “reasonable” amount of time. For the case of this thesis, such a period of time would be on the order of several hundred angstroms of film grown in minutes.

1.3.2.3 Spin Rate

The use of a spin mechanism to affect the reaction rate of the substrate was another consideration. To optimize the adsorption rate of lanthanum sulfide on the surface of a film, the substrate should be fully wetted with a layer of liquid film at all times. This is easier to achieve at relatively slower spin rates. By keeping the entire substrate wetted at all times, a more uniform film can be achieved. However, the spin rate should also be high enough that the solution is constantly refreshed with solution from the reactor. In this way, the amount of lanthanum sulfide in solution can be kept relatively high, increasing the rate of reaction.

1.3.2.4 Reactant Concentrations

There was both an anionic and a cationic reactant used for the process. By lowering the respective reactant concentrations, the reaction rate should decrease. One approach to optimizing this would be to have one relatively low concentration reactant (the limiting reactant) and one reactant in excess. If one reactant is relatively more expensive, this

approach could reduce process costs. However, the stoichiometry of the lanthanum sulfide deposition process is not known, so the extent to which one reactant is the limiting one cannot be determined. For this reason, a ratio of 1:1 lanthanum to sulfide concentration was chosen, and this ratio was kept constant.

Since the deposition time is in the order of minutes, and sometimes seconds, error in deposition times from experiment startup and shutdown should be considered. Such error is estimated to introduce about 5 seconds of error to run times. The reduction of reaction rate therefore could lead to better process control by reducing calculated growth rate error by increasing run times. Lower concentrations may also increase uniformity. Maintaining a low concentration is optimized against the need for a reasonable process time (which would demand higher reactant concentrations).

1.3.2.5 Film Thickness

The film thickness itself can be a parameter which needs to be optimized. The film on the substrate itself can reach such a thickness that it will peel on the macroscopic level. Therefore, it is important to limit growth rate so that the risk of peeling is minimal. This can be achieved by manipulation of all of the previously mentioned optimization parameters (substrate temperature, reactor length, spin rate, reactant concentration). A lower temperature, smaller reactor length, low spin rate, and low reactant concentrations would reduce growth rate per minute.

2. EXPERIMENTAL PROCEDURE

All silicon dioxide coupons were cleaned by sonication in a 1 M sodium hydroxide bath for five minutes. This also served the purpose of making the adsorption of lanthanum sulfide on the substrate surface more favorable. The coupon was then rinsed with deionized water and dried using nitrogen gas. This prepared silicon coupon was placed on a spinning apparatus and secured there using Kapton tape. Then, the two solutions to be used in forming lanthanum sulfide film were prepared. Aqueous 0.025 M $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ was used to provide lanthanum cations and aqueous 0.025 M $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ solution was used to provide sodium anions. 0.006 M solutions of the anionic and cationic precursors were also used for some experiments. The experimental setup is displayed in Figure 2:

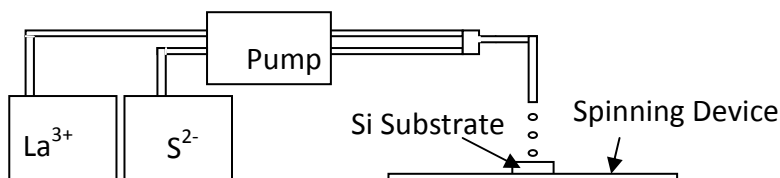


Figure 2: T-mixer Setup for nanocluster deposition experiment

The solutions were simultaneously pumped together to form lanthanum sulfide slurry near the point of film deposition. Film thickness was manipulated in a variety of ways.

By manipulating the amount of applied heat for the process, film thickness could be changed. Experiments were conducted at room temperature, 60 °C, and 100 °C. Likewise, the length of the tube at the exit of the T-mixer could be adjusted, changing the amount of residence time for the reacting solution. Here, tube lengths used were: 10, 20, and 40 cm. All tubing used was 1.22 mm Tygon tubing. All substrate samples were exposed to solution pumped at a rate of either 7.5 mL or 15 mL per minute and spun at various spin rates ranging from 2000 RPM to 7100 RPM. From the flow rate and tube length, residence time has been calculated and included in deposition parameters. For each sample, the film deposition process occurred for variable times between twenty seconds and four minutes.

Energy Dispersive X-ray (EDX) analysis was used to confirm that lanthanum sulfide was deposited on the silicon dioxide substrate. The samples were also analyzed using Scanning Electron Microscopy (SEM). Transmission Electron Microscopy (TEM) and ultraviolet-visible spectrometry (UV-Vis) data was also obtained.

3. RESULTS

3.1 Qualitative Analysis of SEM results

Shown in Figure 3 on the next page are two lanthanum sulfide film samples. In the images provided, films were created at both room temperature and 60 °C. A qualitative comparison of the films shows that the film created at 60 °C encounters a much greater degree of nanocluster development than the film at room temperature. Also, it is evident that neither film is highly uniform or structured. Looking at the SEM film structures, both the film at room temperature and the film at 60 °C have nanoclusters of random orientation. The below SEM samples were taken with 10 cm tube length and 0.94 sec. residence time, and 0.025 M concentrations of solutions. Here, the solution was spun at 7100 RPM.

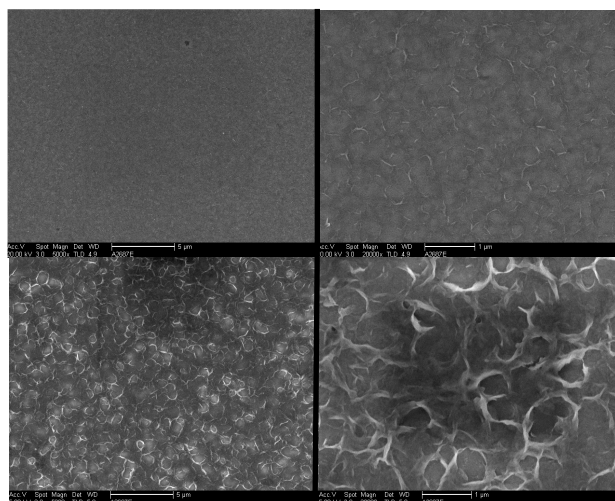


Figure 3: SEM Images of Lanthanum Sulfide. Here, Lanthanum Sulfide film deposited at room temperature at 5 μm (upper left) and 1 μm (upper right) scale. Directly beneath these samples are lanthanum sulfide film deposited at 60 $^{\circ}\text{C}$ at 5 μm (lower left) and 1 μm (lower right) magnification.

3.2 Profilometer Readings on Film Thickness

A profilometer was used to measure the thickness of several of the samples for which film was deposited. A table of the measured changes in film thickness versus reaction time is given below. The samples in Table 1 on the next page were grown at 7100 RPM with 7.5 mL per minute deposition rate.

| Sample # | Film Deposited | Molarity Lanthanum(III) Chloride | Molarity Sodium Sulfide | Time of Substrate's Exposure to Chemical | Temperature | Tube Length | Thickness |
|----------|-------------------|----------------------------------|-------------------------|--|-------------|-------------|---------------|
| 1 | Lanthanum Sulfide | 0.025 | 0.025 | 20 seconds | room temp. | 10 cm | 250 angstroms |
| 2 | Lanthanum Sulfide | 0.025 | 0.025 | 20 seconds | room temp. | 20 cm | 200 angstroms |
| 3 | Lanthanum Sulfide | 0.025 | 0.025 | 20 seconds | room temp. | 40 cm | 400 angstroms |
| 4 | Lanthanum Sulfide | 0.025 | 0.025 | 20 seconds | 60° C | 10 cm | 400 angstroms |
| 5 | Lanthanum Sulfide | 0.025 | 0.025 | 20 seconds | 60° C | 20 cm | 400 angstroms |
| 6 | Lanthanum Sulfide | 0.025 | 0.025 | 20 seconds | 60° C | 40 cm | 400 angstroms |

Table 1: Lanthanum Sulfide Film Thickness Data taken by Profilometer.

Additional samples were prepared at the significantly lower concentration of 0.006 M.

This batch of samples also was deposited at twice the original flow rate (15 mL per minute) to reduce residence time. These samples were prepared at various temperatures, as can be seen in Table 2 on the next page. All of these samples were grown with a spin rate of 2000 RPM.

| Sample # | Film Deposited | Molarity Lanthanum(III) Chloride | Molarity Sodium Sulfide | Time of Substrate's Exposure to Chemical | Temperature | Tube Length | Thickness |
|----------|-------------------|----------------------------------|-------------------------|--|-------------|-------------|----------------|
| 1 | Lanthanum Sulfide | 0.006 | 0.006 | 30 seconds | room temp. | 20 cm | 400 angstroms |
| 2 | Lanthanum Sulfide | 0.006 | 0.006 | 1 minute | room temp. | 20 cm | 1000 angstroms |
| 3 | Lanthanum Sulfide | 0.006 | 0.006 | 2 minutes | room temp. | 20 cm | 2000 angstroms |
| 4 | Lanthanum Sulfide | 0.006 | 0.006 | 2 minutes, 30 seconds | room temp. | 20 cm | 3000 angstroms |
| 5 | Lanthanum Sulfide | 0.006 | 0.006 | 30 seconds | 100° C | 20 cm | 1000 angstroms |
| 6 | Lanthanum Sulfide | 0.006 | 0.006 | 1 minute | 100° C | 20 cm | 1500 angstroms |
| 7 | Lanthanum Sulfide | 0.006 | 0.006 | 1 minute, 30 seconds | 100° C | 20 cm | 3500 angstroms |
| 8 | Lanthanum Sulfide | 0.006 | 0.006 | 2 minutes | 100° C | 20 cm | 3000 angstroms |

Table 2: "Optimal Condition" Lanthanum Sulfide Film Thickness Data

Figure 4 on the next page shows how the thickness readings from Table 2 correlate with time. Looking at the respective growth rates for each temperature, there is a nearly linear trend for film thickness versus time in the case of room temperature deposition. Also, film thickness for the heated substrate samples is higher than for the samples at room temperature, as would be expected.

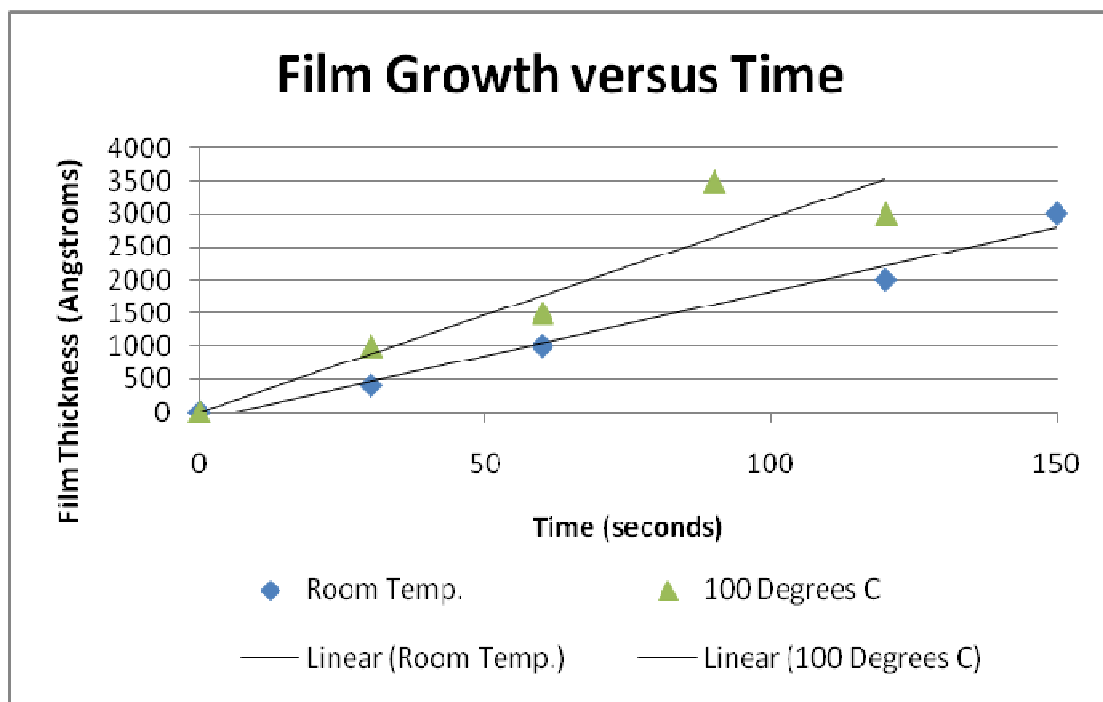


Figure 4: Film Growth Rate versus Time for films grown in Table 2

3.2.1 Profilometer Data for Different Techniques

Three different deposition methods were compared: spin deposition, dipping, and nanocluster deposition. For the spinning and dipping techniques, the 0.05M lanthanum chloride precursor was initially added, followed by 0.05 M sodium sulfide. In between anionic and cationic coatings, DI water was used for rinsing. The key difference between these two techniques is in the dipping method the substrate was manually immersed in corresponding cationic/anionic solutions for 10 seconds with 35 seconds of rinse time. However, in the spinning method, the anionic/cationic solution was sprayed on for 10 seconds and rinsed for 35 seconds at 7100 RPM. For nanocluster deposition,

0.025M concentrations of lanthanum chloride and sodium sulfide were used with 7100 RPM spin rate. Comparing the three methods over 60 seconds of deposition: spinning had a 10.9 angstrom per minute deposition rate, dipping had a 72.7 angstrom per minute deposition rate, and nanocluster deposition had a 750 angstrom per minute deposition rate. Even with higher concentration chemicals for both the spinning and dipping SILAR techniques, the deposition rate is dramatically greater for the nanocluster deposition process than for the SILAR process.

3.3 Ultraviolet-Visible Spectrometry Data

Solutions of the same composition used in the SEM analysis (hydrous 0.025 M lanthanum chloride and 0.025 M sodium sulfide solutions) were mixed together and deposited in a 1 cm cuvette. Once sufficient solution was deposited (within 30 seconds), the solution was analyzed via UV-Vis. From the UV-Vis analysis shown below, lanthanum sulfide material was determined to have a bandgap of 3.5 eV or higher. Table 3 below highlights how bandgap changes over the two different tube lengths, which correspond to two different residence times.

| Tube Length | Bandgap |
|-------------|---------|
| 10 cm | 3.2 eV |
| 20 cm | 3.5 eV |
| 40 cm | 3.5 eV |

Table 3: UV-Vis Bandgaps. Differences in bandgaps shown could be caused by different particle sizes.

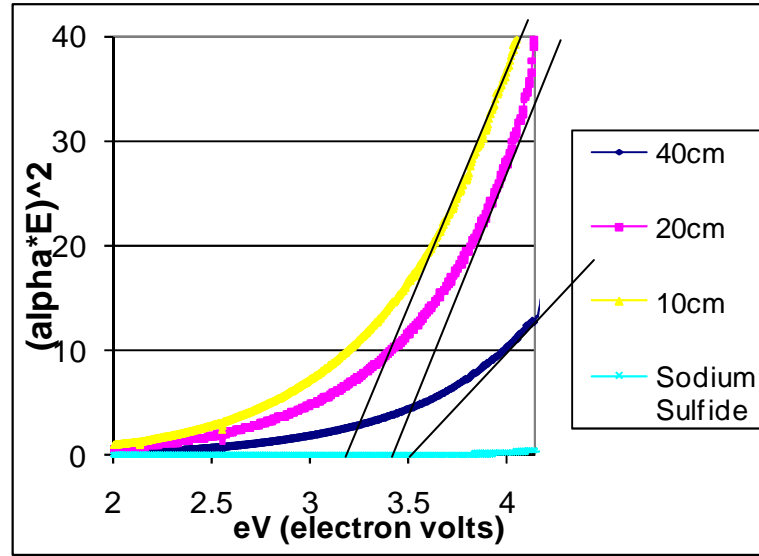


Figure 5: Band-gap Determination from UV-Vis. This figure shows that lanthanum sulfide bandgap changes with increases in particle size.

The determination of the band gaps using Figure 3.3 shown in Table 3 occurs with the use of the following equation³:

$$\alpha = K \frac{(h\nu - E_g)^{1/2}}{h\nu}$$

Here: K represents a constant, α =the absorbance, h =Planck's constant, ν =the frequency, and E_g is the band gap. The energy, E , shown in Figure 5 is equal to $h\nu$.

By going to the point where $\alpha=0$, the band gap can be directly read by extending the linear region of each plot to the x-axis as shown in Figure 5.

3.4 Analysis of TEM Results

Lanthanum Sulfide material was deposited on a lacey carbon control grid for transmission electron microscopy (TEM) analysis. While the substrate was heated for all deposited samples, here the tubes were heated to warm the solution deposited. For the deposition for Figure 6, 0.025 M concentrations of cationic and anionic precursors were used with a 15 mL per minute flow rate at room temperature for 60 seconds. The residence time was 0.94 seconds using a 20 cm piece of tubing. As is seen in Figure 6 on the next page, the lanthanum sulfide material has some amorphous and some polycrystalline regions. Looking at Figure 7 on the next page, TEM analysis indicates that deposited particles range in size from one to fifty nanometers in length. The large range in particle size distribution could indicate that uniformity may be very difficult to achieve for grown films. This was to some degree found to be the case, with few films truly achieving consistent film thickness across the entire coupon.

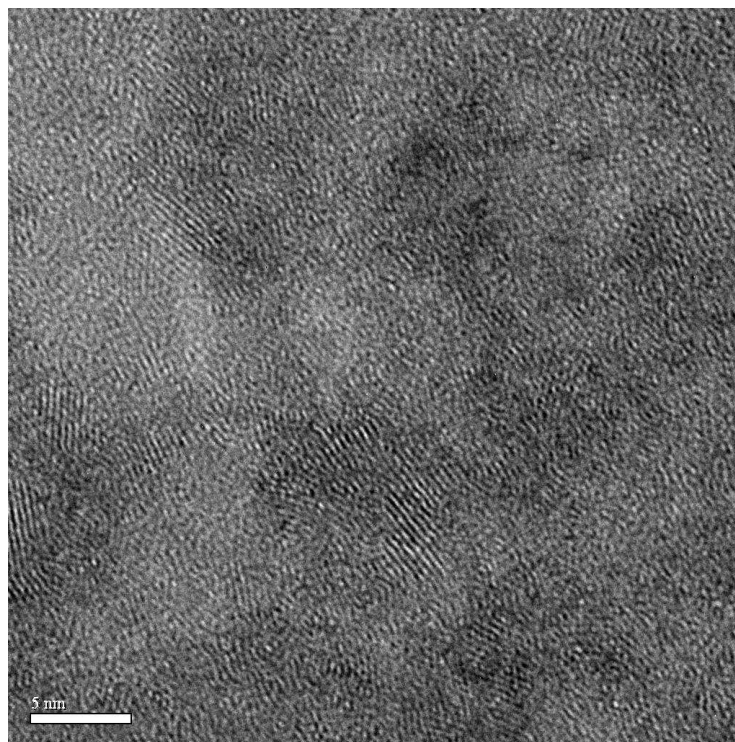


Figure 6: TEM image of lanthanum sulfide material. As can be seen from the image, this material has some polycrystalline regions.

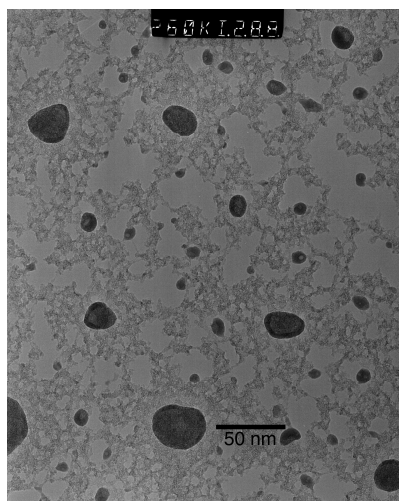


Figure 7: TEM image of lanthanum sulfide particles. These particles range in size from ~ 1 -50 nm. This TEM was prepared using A1 process conditions in Appendix A.

3.5 EDX Data

Energy Dispersive X-ray (EDX) data was used to analyze the overall chemical composition of the deposited films. From the data, it was confirmed that lanthanum and sulfide elements were the great majority of what was deposited. Also, some sodium contaminant from solution was deposited. All copper was from the wire material of the TEM grid. This data confirms deposition of some stoichiometric variant(s) of lanthanum sulfide. For the full set of EDX data, please see Appendix B.

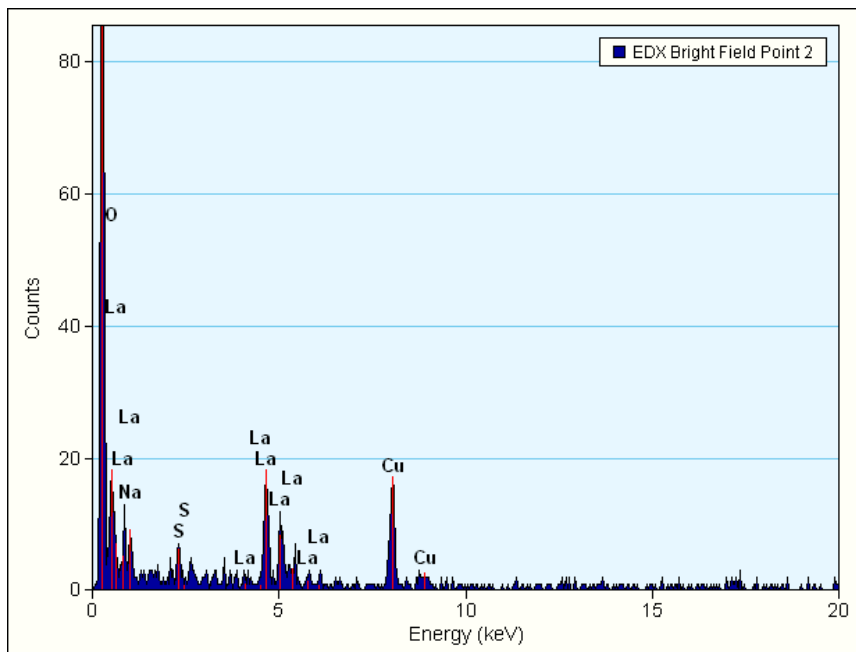


Figure 8: EDX Data. The data above confirm a lanthanum-sulfide compound was actually deposited.

4. CONCLUSIONS

This paper has laid the groundwork for a novel approach for the deposition of lanthanum sulfide nanoparticles on silicon dioxide substrate. This approach could be used as a possible low-cost system for thin film deposition in the future. From SEM data, the films created can be seen qualitatively to be of poor uniformity. As was shown in this study, deposition rate was increased as temperature was increased, and deposition occurred at a nearly linear rate over time for room temperature conditions. As deposition rate increased, poorer uniformity was reached (as shown by SEM). To increase film quality, maintaining this deposition process at room temperature or a lower temperature should improve film uniformity.

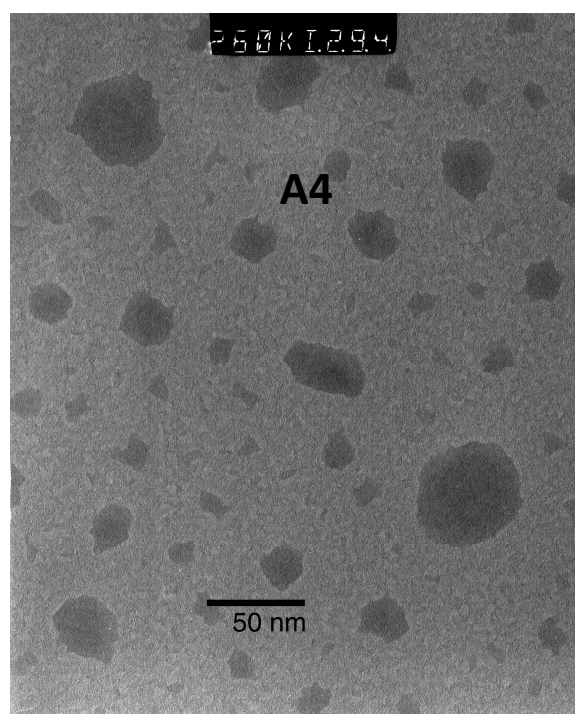
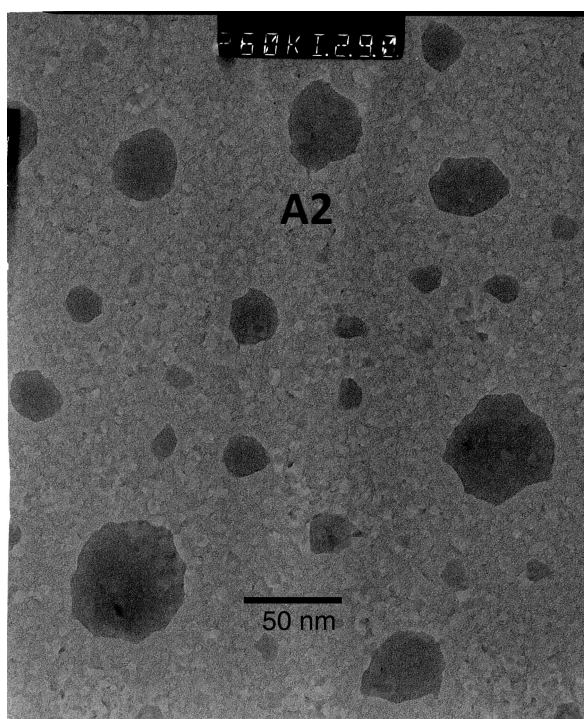
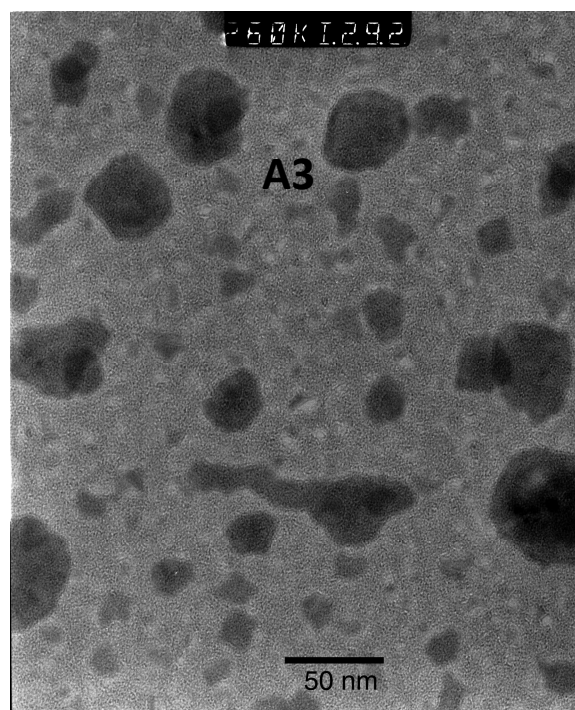
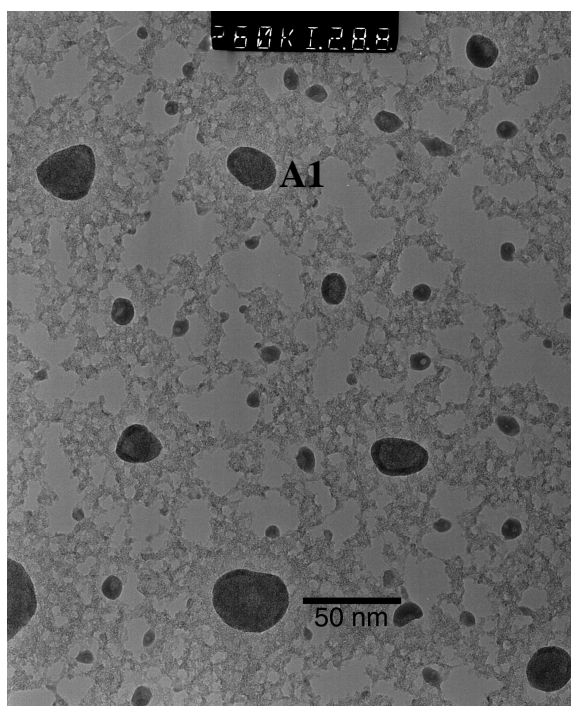
Appendix A

The samples below used 20 cm tubing.

| Overall Results | | | | | | |
|-----------------|-------------------------|-----------------------|----------------------|---------------------------|---------------------------------|---------------------------------|
| TEM Sample # | Reaction Time (seconds) | Residence Time (sec.) | Tube Temp. (Celsius) | Substrate Temp. (Celsius) | LaCl ₃ Conc. (mol/L) | Na ₂ S Temp. (mol/L) |
| A1 | 20 | 2.5 | 60 | Room Temp. | 0.025 | 0.025 |
| A2 | 20 | 2.5 | 60 | 60 | 0.025 | 0.025 |
| A3 | 20 | 2.5 | Room Temp. | 60 | 0.025 | 0.025 |
| A4 | 20 | 2.5 | Room Temp. | Room Temp. | 0.025 | 0.025 |

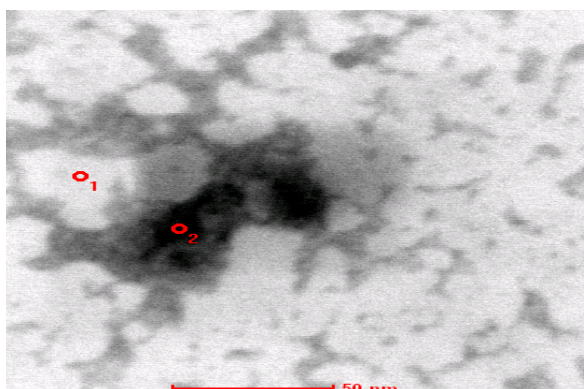
| TEM Sample # | Size |
|--------------|--|
| A1 | Typically small. ~3-50 nm particle range, with mostly 6 nm particles |
| A2 | Much larger particles. Particles typically ~12.5 nm or ~50 nm |
| A3 | Larger particle size. Similar to A2, except some particles are less spherical. |
| A4 | Particles typically ~12.5 nm. ~6.25-50 nm range |

Samples follow on the next page, with: A1 (upper left), A3 (upper right), A2 (lower left), and A4 (lower right)

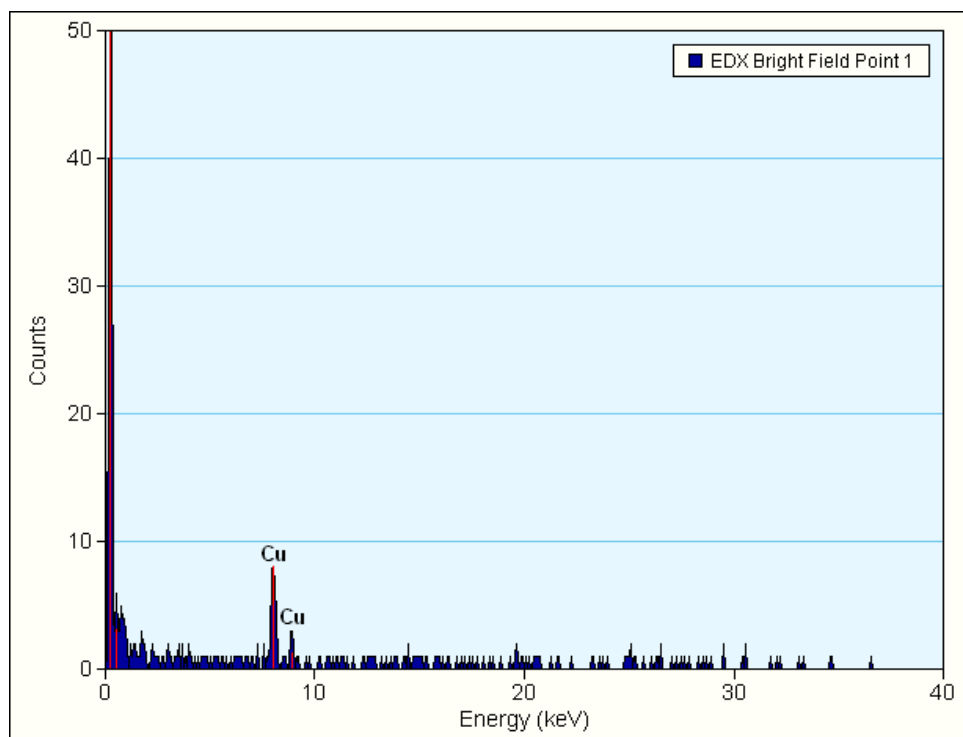


Appendix B

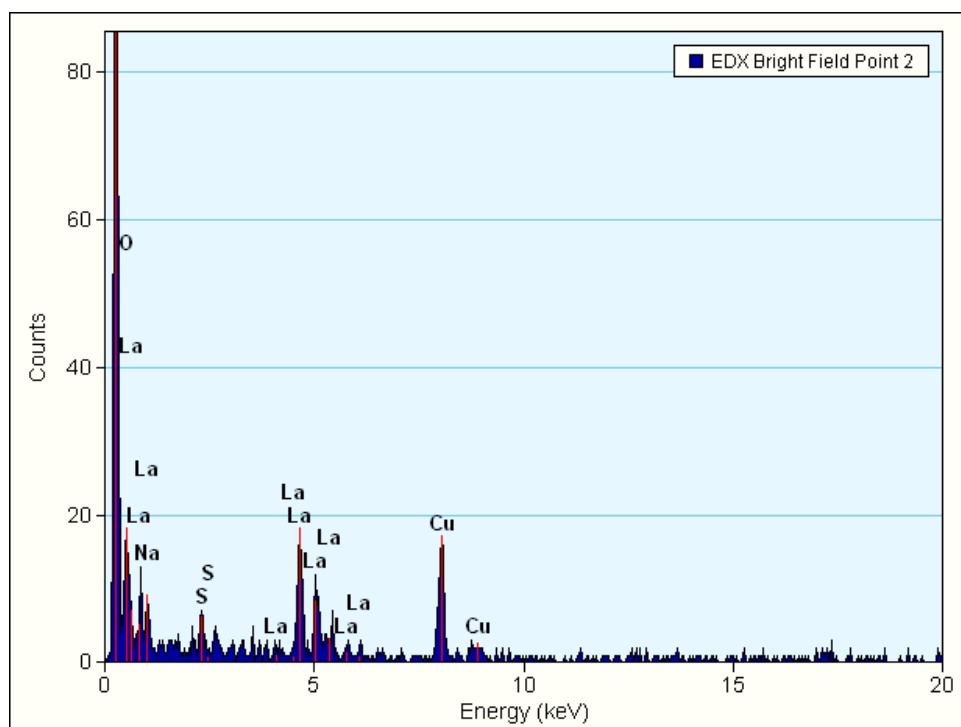
EDX Image (below):



Region 1, without film deposition (blank) (below):



Region 2, with Film Deposition (below):



Bibliography:

1. Lu Tian et al. *Journal of Materials Chemistry* 16 (2006). p. 272-277.
2. Kaupo Kukli et al. *Journal of Alloys and Compounds* 275-277 (1998). p. 10-14.
3. G.D. Bagde, S.D. Sartale and C.D. Lokhande. *Thin Solid Films* 445 (2003). p. 1-6.
4. Puurunen, Riikka L. *J. Appl. Phys.* **97**, 121301 (2005) (52 pages).
5. Pillai, P. K. Vidyadharan and K. P. Vijayakumar. *Solar Energy Materials and Solar Cells* **51**, (1998) 47-54.
6. Pathan, H.M. and C. D. Lockhande. *Bull. Mater. Sci.*, Vol. 27, No.2 (2004), p. 85-111.
7. Hodes, Gary. Chemical Solution Deposition of Semiconductor Films. New York: Marcel Dekker. 2003.
8. Fairchild, S. and J. Jones. *J. Vac. Sci. Technol.* B 23. January/February 2005.
9. J. Antony et al. *Applied Physics Letters* **87**, 241917 (2005).
10. Ohring, Milton. *Materials Science of Thin Films*. San Francisco: Academic Press. 2002.