Morphological and Compositional Analysis of Electrodeposited Indium (III) Sulfide (In$_2$S$_3$) Films

Maqsood Ali Mughal$^a$, M. J. Newell$^b$, Joshua Vangilder$^a$, Shyam Thapa$^a$, Kayla Wood$^b$, Dr. Robert Engelken $^{a,b}$, Dr. B. R. Carroll$^c$, and Dr. J. Bruce Johnson$^c$

Arkansas State University, Jonesboro, AR, 72467, USA
($^a$Environmental Sciences Graduate Program, $^b$Electrical Engineering Program, $^c$Physics Program)

Abstract — In the last few years, notable progress in understanding the growth mechanism of thin solar films deposited by numerous techniques have been made. Electrodeposition continues to be a complex deposition technique that can lead to low-quality material regions (crack) in the semiconductor material. Such cracks form porous zones on the substrate and diminish the heterojunction interface quality of a photovoltaic (PV) cell. In this paper, electrodeposition of In$_2$S$_3$ films was systematically and quantitatively investigated by varying the electrodeposition parameters including bath composition, current density, deposition time, and deposition temperature. Their effects upon the film growth mechanism, composition, and morphology were studied with the help of scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and fracture and buckling software (digital image analysis). In addition, the effect of different glass substrates (Mo, ITO, and FTO) and annealing treatments upon the performance of the electrodeposited In$_2$S$_3$ film was analyzed. Furthermore, the Taguchi Method was used to determine the optimal electrodeposition parameters and study their influence upon the morphological and compositional properties of In$_2$S$_3$ films.

Index Terms — electrodeposition, current density, indium sulfide In$_2$S$_3$, photovoltaic cell, Taguchi method.

I. INTRODUCTION

In$_2$S$_3$ is a promising indirect bandgap (2.3 eV) semiconductor material that is applicable for optoelectronic, photovoltaic, and photoelectric devices [1]. In$_2$S$_3$ has been used as an alternative to CdS as a buffer layer in copper indium gallium selenide/sulfide (CIGS)-based solar cells [2]. Several reports have been published on deposition of In$_2$S$_3$ thin films with diverse morphologies by numerous deposition techniques. In$_2$S$_3$-based CIGS solar cells, efficiencies of 15.7% have been achieved, which is slightly less than the 16% efficiency reported for CdS-based solar cells deposited by chemical bath deposition (CBD) [3].

Electrodeposition is considered to be a low-cost alternative to vacuum-based technique for applying thin films to a substrate with full coverage and high growth yield. It provi
to a substrate with full coverage and high growth yield. It provides high material utilization efficiency and precise control with proper bath chemistry [4] [5]. Electrodeposited In$_2$S$_3$-based CIGS$_e$ solar cells have yielded the highest efficiency of 10.2% [6]. However, electrodeposition still remains a complex technique for synthesizing thin solar films due to several deposition parameters which can affect the properties of the films. Poor adhesion, non-uniformity, flaking, and cracking of films are common problems when electrodepositing thin films onto smooth surfaces, as nucleation growth is influenced by various deposition parameters and contamination of the surface [7] [8]. In view of this, an effort has been made to study the morphological and compositional properties of electrodeposited In$_2$S$_3$ films.

In this paper, we present studies on electrodeposition of In$_2$S$_3$ films using an organic solvent, ethylene glycol. The morphological and compositional properties of In$_2$S$_3$ films were analyzed by varying deposition parameters including bath composition, current density, deposition time, and deposition temperature. In addition, the stoichiometric ratio between sulfur and indium was tailored to the optimal ratio by providing annealing treatment. In$_2$S$_3$ films were deposited onto three different substrates namely indium tin oxide (ITO), fluorine-doped tin oxide (FTO), and molybdenum (Mo)-coated glass substrates, to study their effects upon the morphology and composition with respect to the crack density and stoichiometry of the films. The statistical Taguchi Method was used to obtain optimal deposition parameters based upon the data obtained from scanning electron microscopy (SEM), digital image (from SEM) analysis (using fracture and buckling software), and energy dispersive X-ray spectroscopy (EDS). The primary goal was to avoid non-uniformity, cracks, and improper stoichiometry.

Taguchi (statistical) analysis helped us to analyze the effect of each deposition parameter upon the morphological and compositional properties of the In$_2$S$_3$ films.

II. EXPERIMENTAL DETAILS

The electrodeposition was performed in an electrochemical cell using Ag/AgCl reference electrode, cathode (glass substrate), and anode (graphite). Voltage and current was applied to the electrodes to deposit the material onto the substrates.

An electrolytic solution was prepared containing 150 ml of ethylene glycol (C$_3$H$_8$O$_2$), 0.1 M sulfur (S), 0.1 M sodium chloride (NaCl), and 0.05 M indium chloride (InCl$_3$). S was dissolved in (C$_3$H$_8$O$_2$) by heating the solution to 150 °C. After
S melted and fully dissolved, the solution was cooled down to 80 °C, and then InCl₃ and NaCl was added to solution. Later, sodium thiosulfate (Na₂S₂O₅·5H₂O) was added to solution and used as an additional source of sulfur. A digital potentiostat (WaveNow) from Pine Research Instrumentation was used in a galvanostat mode to perform chronopotentiometry (supplying voltage and current). The substrates were thoroughly cleaned in soapy water and then ultrasonically treated in distilled water for 45 minutes at high temperature. In₂S₃ films were deposited over 3.75 cm² surface area of the substrate.

### III. ANALYSIS AND RESULTS

#### A. Statistical Analysis

The electrodeposited In₂S₃ films were statistically analyzed using Minitab 16. The Taguchi analysis was performed to optimize electrodeposition parameters in order to improve the morphology and composition of In₂S₃ films. The analysis helped us to analyze the effect of each deposition parameter upon the performance of the electrodeposited material.

Table I lists the deposition parameters and their levels involved in the study. The values of the levels were changed to study the effects of individual deposition parameters upon the responses, with the least number of experimental runs. The crack density was chosen as a signal factor (response) in this study. Later, the stoichiometric ratio between sulfur and indium was studied as a function of annealing temperature to achieve the proper stoichiometry. An orthogonal array (design of experiments DOE) of L₁₈ (2¹ x 3⁴) was selected for conducting experiments at two and three levels for bath composition and the rest of the four deposition parameters. Therefore, 18 experiments were performed to complete the study. For each experiment, two samples were generated to minimize the error in the data and achieve balance in the DOE. The effect of each deposition parameter at a given level upon the response was estimated using analysis of means (ANOM and analysis of variance (ANOVA).

![Fig.1. Optimal Deposition Parameters](image)

**TABLE I**

CONTROL DEPOSITION PARAMETERS AND LEVELS FOR THE ELECTRODEPOSITION OF IN₂S₃ FILMS

| Levels | Deposition Parameters | Levels | Deposition Parameters |
|--------|-----------------------|--------|-----------------------|
| 1      | “A” Bath Composition  | 2      | “B” Current Density    |
| 2      |                       | 3      | “C” Substrate          |
| 3      |                       | 4      | “D” Deposition Time    |
| 4      |                       | 5      | “E” Deposition Temperature |

| gehören “A” Bath Composition | “B” Current Density (mA/cm²) | “C” Substrate | “D” Deposition Time (min) | “E” Deposition Temperature (°C) |
|------------------------------|------------------------------|---------------|--------------------------|-------------------------------|
| 1 0.1M S + 0.05M InCl₃ + 0.1M NaCl | 0.75 | Mo | 5 | 140 |
| 2 0.1M S + 0.1M Na₂S₂O₅·5H₂O +0.05 M InCl₃ + 0.1M NaCl | 1.25 | ITO | 10 | 150 |
| 3 ---- | 1.75 | FTO | 15 | 160 |


### Table II

**RESPONSE TABLE FOR MEANS**

(MEAN CRACK DENSITY)

| Levels | A. Bath Composition | B. Current Density (mA/cm²) | C. Substrate | D. Deposition Time (min) | E. Deposition Temperature (°C) |
|--------|---------------------|-----------------------------|--------------|--------------------------|-------------------------------|
| 1      | 0.1989              | 0.0684                      | 0.16         | 0.1880                   | 0.1284                        |
| 2      | 0.1772              | 0.2847                      | 0.2721       | 0.2002                   | 0.2232                        |
| 3      | ---                 | 0.1916                      | 0.1758       | 0.1754                   | 0.2005                        |
| ▲      | 0.0218              | 0.2162                      | 0.1121       | 0.2474                   | 0.0948                        |
| Rank   | 5                   | 1                            | 2            | 4                        | 3                             |

**B. Digital Image Analysis**

In the past, our electrodeposited In₂S₃ films have shown good stoichiometries but poor morphologies [9]. Films were usually non-uniform and thicker around the edges, and sometimes flaked away into the solution when pulled out from the electrochemical cell. The films have shown cracks, which form porous zones on the substrate and could possibly result in loss of charged carriers and insufficient electrical transport within the PV cells [9] [10].

To study the crack behavior as a function of deposition parameters, digital image analysis of SEM images was performed using fracture and buckling analysis software. This software runs on a program that has been written using MATLAB Version 7.1 (R14). It investigates and detects the dark features of the image compared to the average intensity of the image. The crack density is determined by linear analysis. A line pattern (over the selected area of interest) is superimposed onto the SEM image, where this line pattern is perpendicular to cracks. The intersection between the analysis lines and cracks are determined [11]. Hence, the crack density is determined by dividing the number of intersections with the cumulative line length, as shown in Fig.2.

Hence, SEM images (with same magnification scale, 5 kX) were taken for all In₂S₃ films to calculate crack density (number of cracks/54.9742 µm square). The mean crack density for films deposited at current density of 0.75 mA/cm² was 0.0685 cracks/54.972 µm square, whereas, the mean crack density for films deposited at 1.25 mA/cm² and 1.75 mA/cm² were 0.2846 cracks/54.972 µm square and 0.2055 cracks/54.972 µm square, respectively. However, the crack density for films deposited at current density of 1.25 mA/cm² and 1.75 mA/cm² were unknown for four In₂S₃ films. These films were assumed to have high crack densities and, therefore, flaked away from the substrate while rinsing with distilled water after electrodeposition. Similarly, the mean distance between the cracks was found to be 0.9271 µm for films deposited at current density of 0.75 mA/cm², whereas, the mean distance between cracks increased to 3.725 µm and 5.95 µm for films deposited, respectively, at 1.25 mA/cm² and 1.75 mA/cm².

**C. Morphological Analysis**

The cracked morphology of electrochemically deposited In₂S₃ thin films have been reported previously by several scientists, for instance in [12], [13], and [14]. The reason is still misunderstood and not fully known at most times. The potential causes for the cracking behavior of the electrodeposited semiconductor thin films include thickness, poor incorporation of solutes with solvents [15], deposition voltage [16], substrates, surface contamination [17], and piezoelectric effect, current density [18], and electrolytes [19]. In our study, we found that the current density and substrate, respectively, the most and second-most significant deposition parameter responsible for the cracking behavior in electrodeposited In₂S₃ films. Films on FTO- and ITO-coated glass substrates were non-uniform and part of the films flaked away when rinsed with distilled water, whereas the films deposited onto Mo-coated glass substrates were uniform and adherent. However, In₂S₃ films on all three substrates featured cracks and porous zones, as were evident from SEM micrographs (see Fig. 3). Current densities were found to have a significant impact upon the morphology of In₂S₃ films. The mean crack density and mean distance between cracks were significantly higher for films deposited at higher current densities (1.25 mA/cm² and 1.75 mA/cm²) than for films deposited at lower current density (0.75 mA/cm²). The mean distance between the cracks for films deposited at 1.75 mA/cm² was close to 6 µm.

Moreover, the morphology of the In₂S₃ films on ITO glass substrates was also influenced by the substrate itself and the bath composition. The films deposited using sodium thiosulfate as an additional sulfur source showed poor adhesion. Films flaked-off of the substrate after post-deposition rinsing with distilled water. However, films...
deposited using only sulfur showed good adherence, but high crack density. On the other hand, In$_2$S$_3$ film morphology on FTO glass substrate was far better than ITO glass substrates in terms of uniformity (coverage), appearance, and adherence. Current density was the only significant factor affecting the morphology of the films. Meanwhile, molybdenum glass substrates yielded the best-electrodeposited In$_2$S$_3$ films. The films showed nice uniformity and adherence regardless of the bath composition, deposition time, and deposition temperature. High current density (1.25 mA/cm$^2$ and 1.75 mA/cm$^2$) produced films with high crack densities, whereas, low current density (0.75 mA/cm$^2$) produced crack-free In$_2$S$_3$ films (see Fig. 3).

![Crack Density](image1)

**Fig. 3.** Electrodeposited In$_2$S$_3$ film morphology on molybdenum (Mo)-coated, indium tin oxide (ITO), and fluorine-doped tin oxide (FTO) glass substrates at three different current densities.

**D. Compositional Analysis**

According to our previous work, M. A. Mughal, M. J. Newell, R. Engelken, et. al., “Optimization of the electrodeposition parameters to improve the stoichiometry of In$_2$S$_3$ films for solar applications using the Taguchi Method, *Journal of Nanomaterials*, vol. 2014, pp. 1-10, 2014 [10], we stated that deposition voltage has the highest significant impact upon the stoichiometry of In$_2$S$_3$ films. Therefore, in this current study, we found, as expected, the current density (a strong function of deposition voltage) to have a significant impact upon the composition of the films. In$_2$S$_3$ films deposited at low current density produced crack-free films, however, the composition of the films was slightly sulfur-rich as-deposited (see Table III). Subsequently, In$_2$S$_3$ films were annealed at 250 °C for an hour in air to evaporate the excess sulfur. After the annealing treatment, the stoichiometric ratio between sulfur and indium was nearly perfect (S/In : 3/2).

**IV. SUMMARY OF WORK**

In$_2$S$_3$ was electrodeposited onto Mo-coated glass substrates using an organic solvent. In$_2$S$_3$ films with planar surface morphologies and near-to-perfect stoichiometric ratios were successfully deposited. Morphological and compositional properties of In$_2$S$_3$ were studied by varying deposition parameters. Current density had the most significant impact upon the morphology and composition of films. In$_2$S$_3$ films deposited at low current density (0.75 mA/cm$^2$) produced uniform, adherent, and crack-free films. In our intensive study, we observed that the In$_2$S$_3$ films tend to start cracking from the edge of the substrate. The nucleation growth is higher near the edges and therefore films initially start to flake-off from the edge of the substrate. As the current density/deposition time increases, those cracks tend to propagate into the middle part of the substrate and, eventually, the film either falls into the solution while pulling-off the substrate or flakes-off while rinsing with distilled water. The films deposited on FTO-glass substrates also showed nice morphology at low current density, while films on ITO-glass substrates showed poor uniformity and adherence at all levels. This indicates that the different substrates can also lead to different morphologies with the same deposition parameters. The Taguchi Method helped us to optimize the deposition parameters and understand their influence upon the cracking behavior of the In$_2$S$_3$ films. The mean crack density and the mean distance between the cracks increased approximately by 400- and 600 times for the films grown at higher current density for all three substrates. Similarly, composition of the films was highly influenced by the current density. However, In$_2$S$_3$ films electrodeposited at low current density produced slightly sulfur-rich films, which were then annealed for an hour at 250 °C. After the annealing treatment, excess sulfur was removed.
and the stoichiometry between sulfur and indium was near-to-perfect (S/In : 3/2).

ACKNOWLEDGEMENTS

The authors acknowledge the gracious support provided by Arkansas State University, National Science Foundation grant EPS-1003970 administered by the Arkansas Science and Technology Authority, and NASA grant NNX09AW22A administered by the Arkansas Space Grant Consortium. Dr. Alan Mantooth, Kathy Kirk, Dr. Greg Salamo, Dr. Omar Mansareh, Dr. Alex Biris, Dr. Tansel Karabacak, Dr. Hyewon Seo, and other collaborators at the University of Arkansas (Fayetteville, Little Rock, and Pine Bluff campuses) are also thanked, as are Dr. Keith Hudson and Laura Holland at ASGC, and Dr. Gail McClure, Cathy Ma, and Marta Collier at ASTA.

REFERENCES

[1] A. Dutta, S. K. Panda, S. Gorai, D. Ganguli, S. Chaudhuri, “Room temperature synthesis of In$_3$S$_3$ micro- and nano-rod textured thin films,” *Materials Research Bulletin*, vol. 43 (4), pp. 983-989, 2008.

[2] N. A. Allsop, A. Schönmann, H. J. Muffler, M. Bär, M. C. Lux-Steiner, and Ch. H. Fischer. “Spray-ILGAR indium sulfide buffers for Cu(In,Ga)(S,Se)$_2$ solar cells,” *Progress in Photovoltaics: Research and Applications*, vol. 13, pp. 607-616, 2005.

[3] R. Jayakrishnan, T. T. John, C. S. Kartha, K. P. Vijayakumar, T. Abe, and Y. Kashiwaba, “Defect analysis of sprayed β-In$_3$S$_3$ thin films using photoluminescence studies,” *Semiconductor Science and Technology*, vol. 20, 1162, 2005.

[ref1] J. S. Wellings, A. P. Samantilleke, S. N. Heavens, P. Warren, and I. M. Dharmadasa, “Electrodeposition of CulnSe$_2$ from ethylene glycol at 150 °C,” *Solar Energy Materials and Solar Cells*, vol. 93 (9), pp. 1518–1523, 2009.

[ref2] M. J. Newell, M. A. Mughal, R. Engelken, et. al., “Elemental sulfur-based electrodeposition of indium sulfide films,” 37th *IEEE Photovoltaic Specialists Conference (PVSC)*, Seattle, WA, pp. 1322-1326, June 19-24, 2011.

[4] X. Sheng, L. Wang, G. Chen, and D. Yang, “Simple synthesis of flower like In$_3$S$_3$ structures and their use as templates to prepare CuS particles,” *Journal of Nanomaterials*, vol. 2011, pp. 5-10, 2010.

[5] N. Naghavia, E. Chassising, S. Galanti, G. Renou, M. Soro, M. Bottemy, A. Etcheberry, and D. Lincot, “Electrodeposition of In$_3$S$_3$ buffer layer for Cu(In,Ga)Se$_2$ solar cells,” *European Materials Research Society Conference Symposium, Advanced Inorganic Materials and Concepts for Photovoltaics, Electrochemical Society*, vol. 10, pp. 155-160, 2012.

[6] D. Lincot, “Electrodeposition of semiconductors,” *Thin Solid Films*, vol. 487, pp. 40-48, 2005.

[7] M. Lajnef and H. Ezzaaouia, “Structural and optical studies of indium sulfide thin films prepared by sulfurization of indium thin films,” *The Open Applied Physics Journal*, vol. 2, pp. 23-26, 2009.

[8] M. A. Mughal, M. J. Newell, R. Engelken, et. al., ”Statistical analysis of Electroleplated indium (III) sulfide (In$_3$S$_3$) films, a potential buffer material for PV (Heterojunction Solar Cell) systems, using organic electrolytes,” *Nanotechnology 2013: Bio Sensors, Instruments, Medical, Environment, and Energy*, 3.

Technical Proceedings of the 2013 NSTI Nanotechnology Conference, Washington, DC, pp. 523-527, May 12-16, 2013.

[10] M. A. Mughal, M. J. Newell, R. Engelken, et. al., “Optimization of the electrodeposition parameters to improve the stoichiometry of In$_3$S$_3$ films for solar applications using the Taguchi Method,” *Journal of Nanomaterials*, vol. 2014, pp. 1-10, 2014.

[11] S. Frank and R. Spolenak, “Determination of crack and buckle density by digital image analysis,” Laboratory for Nanometallurgy, ETH Zurich, Switzerland. Available at: http://www.mathworks.com/matlabcentral/fileexchange

[12] A. M. Abdel Haleem, M. Ichimura, “Electrochemical deposition of indium sulfide thin films using two-step pulse biasing,” *Thin Solid Films*, vol. 516, pp. 7783-7789, 2008.

[13] A. M. Abdel Haleem, M. Sugiyama, and M. Ichimura, “Sulfurization of the electrochemically deposited indium sulfide oxide thin film and its photovoltaic applications,” *Materials Sciences and Applications*, vol. 3, pp. 802-806, 2012.

[14] R. S. Mane and C.D. Lokhande, “Studies on Structural, Optical, and Electrical Properties of Indium Sulfide Thin Films,” *Materials Chemistry and Physics*, vol. 78, pp. 15–17, 2002.

[15] G. F. Fulop and R. M. Taylor, “Electrodeposition of semiconductors,” *Annual Review of Material Science*, vol. 15, pp. 197-210, 1985.

[16] A. S. Baranski, W. R. Fawcett, and C. M. Gilbert, “The structural and compositional characterization of bismuth sulfide films grown by cathodic deposition,” *Journal of the Electrochemical Society*, vol. 154 (12), pp. D669-D673, 2007.

[17] M. N. Mammadov, A. Sh. Aliyev and M. Elrouby, “Electrodeposition of cadmium sulfide,” *International Journal of Thin Films Science and Technology*, vol. 2, pp. 43-53, 2012.

[18] V. S. Saji, S-M. Lee, and C. W. Lee, “CIGS Thin Film Solar Cells by Electrodeposition,” *Journal of the Korean Electrochemical Society*, Vol. 14 (2), pp. 61-70, 2011.

[19] S. J. Abbas, “The optical properties of cadmium sulfide thin film prepared by electrochemical deposition technique,” *Basrah Journal of Science*, vol. 25 (2), pp. 1-11, 2007.