Morphological and Compositional Analysis of Electrodeposited Indium (III) Sulfide (In_2S_3) Films

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Within the last few years, there has been notable progress in understanding the growth mechanisms of semiconductor thin films for photovoltaic (PV) applications. Electrodeposition continues to be a complex deposition technique that can lead to regions of low quality (for example, cracks) in films. Such cracks can form porous zones on the substrate and diminish the heterojunction interface quality of a PV cell. In this paper, electrodeposition of In_2S_3 films was systematically and quantitatively investigated by varying electrodeposition parameters including bath composition, current density, deposition time, and deposition temperature. Their effects upon the morphology, composition, and film growth mechanism were studied with the help of scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and digital imaging analysis (using fracture and buckling analysis software). In addition, the effect of different annealing treatments (200°C, 300°C, and 400°C in air) and coated glass-substrates (Mo, ITO, and FTO) upon the properties of the In_2S_3 films was analyzed. Furthermore, the Taguchi/Design of Experiments (DOE) Method was used to determine the optimal electrodeposition parameters in order to improve the properties.

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Indium (III) sulfide (In_2S_3) is a promising semiconductor material (III-VI compound), suited for many technological applications like optoelectronic,¹ photovoltaic,² and photoelectric devices³ due to its stability, large energy bandgap (~ 2.3 eV), and photoconductive behavior.⁴ $\beta\text{-In}_2\text{S}_3$ is an n-type semiconductor material that has been considered as a non-toxic substitute for cadmium containing PV cells.⁵ It has potential to replace cadmium sulfide (CdS) as a buffer layer in copper indium gallium selenide/sulfide (CIGS)-based PV cells due to environmental concerns.⁶ Several reports have been published on synthesis of In_2S_3 films by numerous deposition techniques. These films have exhibited diverse morphologies and structural properties.^{7–11} In In_2S_3 (from atomic layer deposition)-based CIGS PV cells, an efficiency of 16.4%¹² has been achieved, which is few percent less than the 20.8% efficiency reported for CdS-based CIGS PV cells with the CdS deposited by chemical bath deposition (CBD).¹³

Electrodeposition is considered an economical and time-saving alternative to vacuum-based techniques for depositing semiconductor thin films onto a substrate with full coverage and high growth yield.¹⁴ It offers high material utilization efficiency, precise control with proper bath chemistry, and in-situ monitoring.^{14,15} In 2011, electrodeposited In_2S_3 -based CIGSe PV cells yielded an energy conversion efficiency of 10.2%.¹⁶ However, electrodeposition still remains a complex technique for synthesizing thin films due to several deposition parameters, which can affect the properties of the films.^{17,18} Poor adhesion, non-uniformity, flaking, and cracking¹⁹ of films are common problems when electrodepositing films onto smooth surfaces,¹⁴ as nucleation and growth are influenced by various deposition parameters,¹⁵ surface roughness, and contamination of the surface.¹⁷

Synthesizing thin films via solution deposition techniques like electrodeposition has the potential for crack formation, pinholes, or blisters resulting from larger deposition rate,²⁰ mass transport,²¹ thickness,²² etc. In the past, a number of authors have reported issues related to poor adherence, homogeneity,³ uniformity,^{3,18} cracks, or pinholes,^{23–25} which occurs regularly in In_2S_3 films synthesized by solution-based deposition techniques. In our previous work,²⁵ electrodeposited In_2S_3 films featured cracks and porous zones that can diminish the heterojunction interface quality of a PV cell. The nucleation growth was higher near the edges, and, therefore, we observed that the In_2S_3 films tended to start cracking from the edge of the substrate and eventually flake-off. As the current density/deposition time

increased, those cracks tended to propagate into the middle part of the film and, eventually, the film either fell into the solution while pulling-out the substrate, or flaked-off while rinsing with distilled water.

In view of this, an effort has been made to study the morphological and compositional properties of electrodeposited In_2S_3 films, and understand the underlying growth mechanism. Electrodeposition was performed in an ethylene glycol-based electrolytic solution. The morphological and compositional properties of In_2S_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 studied as a function of annealing temperature. The primary goals were to avoid non-uniformity, cracks, and improper stoichiometry. In_2S_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 Taguchi Method was used to determine the optimal electrodeposition parameters based upon the data obtained from scanning electron microscopy (SEM), digital imaging analysis (using fracture and buckling analysis software), and energy dispersive X-ray spectroscopy (EDS). The Taguchi Method is an excellent statistical tool to determine the optimal processing parameters and improve the quality of the product, while lowering the ultimate cost through efficient material use and design of experiments (DOE).²⁶ Today, it is used with great success in industry (pharmaceutical, agriculture, photovoltaic, etc.) to design experiments for problems with multiple process parameters due to its high practicality and robustness.²⁷ With this method we were able to efficiently determine the effect of each electrodeposition parameter upon the morphological and compositional properties of the In_2S_3 films.

Experimental

Electrodeposition was performed in a three-electrode electrochemical cell (a glass beaker) using a Ag/AgCl reference electrode, cathode (coated-glass substrate, 3 mm thick with target resistivity value of 10–25 Ω/sq), and anode (graphite). Figure 1 shows the schematic diagram of an electrochemical cell.

An electrolytic solution containing 150 ml of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), 0.1 M elemental sulfur (S), 0.1 M sodium chloride (NaCl), and 0.05 M indium chloride (InCl_3) was prepared. S was dissolved in

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Figure 1. The schematic diagram of an electrochemical cell.

the substrates were thoroughly cleaned in soapy water (using Comet cleaner) with the help of a toothbrush, and then ultrasonically treated (using a Cole Parmer 8890 Ultrasonic cleaner) in distilled water for 45 minutes at 40°C to remove surface contamination. Finally, substrates were rinsed in an acetone solution and dried under flowing air. In_2S_3 films were deposited over the 3.75 cm² (length: 2.5 cm; width: 1.5 cm) submerged surface area of the glass substrate.

Result Analysis and Discussion

Statistical analysis.— In_2S_3 films were quantitatively analyzed using Minitab 16 statistical software to perform Taguchi analysis, which helped us to optimize the electrodeposition parameters in order to improve the morphology and composition. Table I lists the deposition parameters and their levels involved in the study. The values of the levels (variables) were varied to measure the effect of individual deposition parameters upon the output response (mean crack density, # of cracks/μm), with the least number of experimental runs.

An orthogonal array (design of experiments (DOE)) of L_{18} ($2^1 \times 3^4$) was selected for conducting experiments, meaning, 2 levels for bath composition, and 3 levels each for the other deposition parameters. For each experiment, 2 samples were generated to minimize the error in the data and achieve balance in the DOE. Therefore, 36 (18×2) experiments were performed to complete the study as shown in Table II. The effect of each deposition parameter at a given level upon the output response was estimated using analysis of means (ANOM) and analysis of variance (ANOVA).

Table I. Control Deposition Parameters and Levels for the Electrodeposition of In_2S_3 Films.

Levels	Deposition Parameters				
	"A" Bath Composition	"B" Current Density (mA/cm ²)	"C" Substrate	"D" Deposition Time (min)	"E" Deposition Temperature (°C)
1	0.1 M S + 0.05 M InCl_3 + 0.1 M NaCl	0.75	Mo	5	140
2	0.1 M S + 0.1 M $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ + 0.05 M InCl_3 + 0.1 M NaCl	1.25	ITO	10	150
3	—	1.75	FTO	15	160

Table II. Taguchi Orthogonal Array L_{18} ($2^1 \times 3^4$) Design of Experiments (DOE).

Exp. No.	Deposition Parameters					Output Response	
	"A" Bath Composition	"B" Current Density (mA/cm ²)	"C" Substrate	"D" Deposition Time (min)	"E" Deposition Temperature (°C)	Mean Crack Density (MCD, # of Cracks/μm)	Mean Distance Between the Cracks (MDC, μm)
1	S	0.75	Mo	5	140	0	0
2	S	0.75	ITO	10	150	0.27	3.71
3	S	0.75	FTO	15	160	NF	NF
4	S	1.25	Mo	5	150	0.26	3.93
5	S	1.25	ITO	10	160	0.27	4.11
6	S	1.25	FTO	15	140	0.22	4.65
7	S	1.75	Mo	10	140	0.12	9.77
8	S	1.75	ITO	15	150	0.28	3.62
9	S	1.75	FTO	5	160	0.17	5.78
10	S+ $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	0.75	Mo	15	160	0	0
11	S+ $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	0.75	ITO	5	140	NF	NF
12	S+ $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	0.75	FTO	10	150	0	0
13	S+ $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	1.25	Mo	10	160	0.36	2.76
14	S+ $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	1.25	ITO	15	140	NF	NF
15	S+ $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	1.25	FTO	5	150	0.32	3.17
16	S+ $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	1.75	Mo	15	150	0.21	4.92
17	S+ $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	1.75	ITO	5	160	NF	NF
18	S+ $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	1.75	FTO	10	140	0.17	5.74

*NF: No film

Figure 2. Optimal electrodeposition parameters (A2, B1, C1, D3, E1) from Taguchi Analysis: Main effects plot for means (mean crack density MCD (# of cracks/ μm)).

Figure 3. Digital imaging analysis: Fracture and buckling analysis software for crack density calculation. (Experiment 7, Sample 1).

The main effects plot for means (mean crack density) revealed the optimal values for each electrodeposition parameter, as shown in Figure 2. The points (triangle shape) in the plot are the mean of the output response (crack density) at different levels for each parameter, with a reference line (horizontal dashed line) drawn at the grand mean of the output response. The lowest average mean of mean crack density defines the optimal level (encircled) for that deposition parameter. Therefore, according to the main effects plot for means, the optimal electrodeposition parameters were A2, B1, C1, D3, and E1. It was also evident from the output response table that current density was the most, while bath composition was the least, significant deposition parameter, to the morphology of In_2S_3 films, as shown in Table III. The substrate and deposition temperature were the second- and third- most significant deposition parameters relative to cracks in In_2S_3 films. We also believe that when a thin film was electrodeposited on a thick substrate at an elevated temperature, and subsequently cooled at ambient temperature, the difference between the thermal expansion coefficients of the substrate and In_2S_3 film created stress and strain, further contributing to cracks in the films.

Digital imaging analysis.— In the past, our electrodeposited In_2S_3 films have shown good stoichiometries but poor morphologies.^{18,19} Films were usually non-uniform and thicker around the edges, and sometimes flaked away into the solution when pulled from the electrochemical cell. The films have shown cracks, which formed porous zones on the substrate.^{25,28} These regions of low quality could potentially result in the loss of charged carriers and insufficient electrical transport within the PV cells.²⁹

To study the crack behavior as a function of deposition parameters, digital imaging analysis of SEM images was performed using fracture and buckling analysis software.³⁰ This analytical program was written using MATLAB Version 7.1 (R14), which helped us to determine the crack and buckle density at the micro/nano-scale in a reasonable

amount of time with high accuracy. It investigates and detects the dark features of the SEM image (as shown in Figure 3 in small circles) compared to the average intensity of the image in a few minutes time. The crack density is determined by linear analysis. A vertical line (in parallel) pattern over the selected area of interest is superimposed onto the image, where this line pattern is perpendicular to cracks. The intersections between the analysis lines and cracks are determined. Hence, the crack density is determined by dividing the number of intersections with the cumulative line length.³⁰ The dotted square box indicates the area of interest, which is approximately $2100.69 \mu\text{m}^2$ ($54.62 \mu\text{m} \times 38.46 \mu\text{m}$).

SEM images (captured at magnification scale, 5 kX, distance between electron gun and sample (z-value), 11 mm, and accelerating voltage, 20 kV) were taken for all In_2S_3 films to calculate mean crack density (# of cracks/ μm) and mean distance between the cracks (μm) as shown in Table II. The mean crack density for films deposited at a current density of 0.75 mA/cm^2 was $0.0685 \text{ cracks}/\mu\text{m}$, whereas, the mean crack densities for films deposited at 1.25 mA/cm^2 and 1.75 mA/cm^2 were $0.2846 \text{ cracks}/\mu\text{m}$ and $0.2055 \text{ cracks}/\mu\text{m}$, respectively. However, the crack densities for films deposited at current densities of 1.25 mA/cm^2 and 1.75 mA/cm^2 were unknown for four In_2S_3 films due to poor coverage over the substrate. These films were assumed to have high crack densities since they flaked away from the substrate while rinsing with distilled water after electrodeposition.

Similarly, the mean distance between the cracks was higher for films deposited at a current density of 0.75 mA/cm^2 , compared to the mean distances between the cracks for films deposited, respectively, at 1.25 mA/cm^2 and 1.75 mA/cm^2 . This phenomenon corresponds to increased crack density that is associated with decrease in mean distance between the cracks, which is also evident from Figure 4. For example, the film in Experiment 7, with the lowest crack density among all the In_2S_3 films with cracks, exhibited the greatest mean distance between the cracks. Similarly, the films in Experiments 9 and

Table III. Output Response Table for Means (Mean Crack Density).

Levels	Deposition Parameters				
	"A" Bath Composition	"B" Current Density (mA/cm^2)	"C" Substrate	"D" Deposition Time (min)	"E" Deposition Temperature ($^\circ\text{C}$)
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	0.0247	0.0948
Rank	5	1	2	4	3

Figure 4. MATLAB simulation results (for all 18 experiments): Calculated mean crack density (MCD, # of cracks/ μm) and mean distance between the cracks (MDC, μm) using fracture and buckling analysis software. NF: No film.

18 had greater mean distances between the cracks due to lower crack densities.

Morphological analysis.— The cracked morphology of electrochemically deposited In_2S_3 thin films has been reported previously;^{3,31,32} however, the reason for this is still not fully known. The potential causes include thickness, poor incorporation of solutes with solvents,³³ deposition voltage,³⁴ substrates, surface contamination,³⁵ piezoelectric effect, current density, mass transfer,³⁶ and electrolytes.³⁷

In our study, we found that the current density and substrate type, respectively, were the most and second-most significant deposition parameters associated with the cracking behavior. 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 exhibited good uniformity and adherence. However, In_2S_3 films on all three substrates featured cracks and porous zones, as were evident from SEM micrographs shown in Figure 5. Current densities were found to have a significant impact upon the morphology. The porosity of the films increased with higher current density ($>1 \text{ mA}/\text{cm}^2$) due to a larger rate of material growth at the cathode. Moreover, the morphology of the films on ITO glass substrates was also influenced by the substrate itself and the bath composition. In_2S_3 films deposited using $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ as an additional sulfur source exhibited poor adhesion. Films flaked-off of the substrate after post-deposition rinsing. However, films deposited using only elemental sulfur showed good adherence, but large crack density. On the other hand, film morphology on FTO glass substrates was far better than on 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-on-glass substrates yielded the best-electrodeposited In_2S_3 films. The films showed nice uniformity and adherence regardless of the bath composition and deposition temperature. However, deposition time had a significant impact upon the cracking behavior of the films. Longer deposition times (10 and 15 min.) caused films to crack due to greater thicknesses, suggesting thickness as another potential cause for the cracks. Therefore, films were electroplated for only 5 minutes to deposit very thin In_2S_3 films and eliminate cracks. High current density ($1.25 \text{ mA}/\text{cm}^2$ and $1.75 \text{ mA}/\text{cm}^2$) yielded films with high crack densities, whereas, low current density ($0.75 \text{ mA}/\text{cm}^2$) yielded almost crack-free films.

Compositional analysis.— In our previous work,²⁵ we stated that deposition voltage has the most significant impact upon the stoichiometry of In_2S_3 films. Therefore, in this follow-up study, we found, as expected, that the current density (a strong function of deposition volt-

Figure 5. Electrodeposited In_2S_3 film morphology on molybdenum (Mo)-, indium tin oxide (ITO)-, and fluorine-doped tin oxide (FTO)-coated glass substrates at three different current densities: (A) $0.75 \text{ mA}/\text{cm}^2$, (B) $1.25 \text{ mA}/\text{cm}^2$, and (C) $1.75 \text{ mA}/\text{cm}^2$.

age) has a significant impact upon the composition of the films. Films deposited at low current density produced crack-free films; however, the composition was slightly sulfur-rich as-deposited (see Table IV). Subsequently, In_2S_3 films were annealed at different annealing temperatures (200°C , 300°C , and 400°C) for an hour in air to study the effect of annealing and improve the stoichiometry. After annealing, films annealed at 300°C for an hour in air exhibited nearly ideal stoichiometric ratios between sulfur and indium (S/In: 3/2). However, the films contained a higher percentage of oxygen due to oxygen substituting with sulfur to form $\text{In}_2\text{S}_{3-x}\text{O}_x$ during the process.

Summary of Work

Morphological and compositional properties of electrodeposited In_2S_3 films were studied by varying deposition parameters. Digital imaging analysis of SEM images using fracture and buckling analysis software was performed to quantify the cracks in films. The crack density and mean distance between the cracks were calculated and studied

Table IV. EDS Data for In_2S_3 Films Electrodeposited at $0.75 \text{ mA}/\text{cm}^2$.

Element	As-deposited	Annealed 200°C	Annealed 300°C	Annealed 400°C
	Atomic%			
Carbon (C)	24.3	8.93	0	19.36
Oxygen (O)	19.99	32.34	17.85	58.17
Aluminum (Al)	0	0	0	0.19
Sulfur (S)	32.33	34.05	49.21	11.21
Indium (In)	23.38	24.68	32.94	11.08
(S+O)/In Ratio	2.23	2.69	2.03	6.26
S/In Ratio	1.38	1.37	1.49	1.01

as a function of deposition parameters. Using the Taguchi Method, we succeeded in optimizing the electrodeposition parameters and understanding their influence upon the properties of the films, which are important for optimizing the device efficiency. The optimized parameters helped us to improve the morphology and achieve crack-free films with near-to-ideal stoichiometry. Current density was the most significant deposition parameter correlated with cracks in the films, and the compositions of the films were highly dependent upon it. The composition of the bath was the least significant deposition parameter relative to effect upon the morphology and composition.

In_2S_3 films were electrodeposited onto (Mo, ITO, or FTO)-coated-glass substrates using ethylene glycol-based electrolytes, to study their growth behavior and surface morphology. The optimized deposition parameters were sulfur plus sodium thiosulfate-containing electrolytic solutions (A2), 0.75 mA/cm² current density (B1), molybdenum-coated glass substrates (C1), 15 minute deposition time (D3), and 140°C deposition temperature (E1) (as shown in Figure 2). Using optimized deposition parameters, we were able to successfully synthesize In_2S_3 films with planar surface morphologies and nearly ideal stoichiometric ratios. The films were thin, uniform, adherent, homogeneous, and crack-free. In order to reduce the thickness of the films and further avoid cracks, the films were electroplated for only 5 minutes.

Taguchi analysis proved that the current density had the most significant impact upon the morphology and composition of In_2S_3 films. Films synthesized at higher current densities (1.25 mA/cm² and 1.75 mA/cm²) exhibited high crack densities, whereas, at lower current density (0.75 mA/cm²), films exhibited minimal or no cracks. The porosity of the films increased with higher current density due to the larger rate of material growth at the cathode. The mean crack density increased approximately by 400 to 600 times for the films electroplated at higher current densities on all three substrates. The substrate and deposition temperature were the second- and third-most significant deposition parameters correlated with cracks in films. The interaction between the two was also significant, suggesting that the mismatch between the thermal expansion coefficients of the substrate and In_2S_3 film created stress and caused the films to crack. Furthermore, films deposited onto FTO-glass substrates also exhibited nice morphologies at low current density, while films on ITO-glass substrates showed poor uniformity and adherence at all levels. Films exhibited different morphologies on different substrate types, even with the same deposition parameters. The microstructures in films differed from each other in terms of size, orientation, and appearance although they featured cracks, as shown in Figure 5. Similarly, the composition of the films was highly influenced by the current density. Films electrodeposited at low current density yielded slightly sulfur-rich films, which were then annealed for an hour at 300°C. During the annealing treatment, excess sulfur was removed and the stoichiometry between sulfur and indium was nearly ideal (S/In : 3/2).

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