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Research Article

Optimization of the Electrodeposition Parameters to Improve the Stoichiometry of In_2S_3 Films for Solar Applications Using the Taguchi Method

Maqsood Ali Mughal,[1] M. Jason Newell,[1] Joshua Vangilder,[1] Shyam Thapa,[1] Kayla Wood,[2] Robert Engelken,[1,2] B. Ross Carroll,[3] and J. Bruce Johnson[3]

[1] *Environmental Sciences Graduate Program, Arkansas State University, State University, Jonesboro, AR 72467, USA*
[2] *Electrical Engineering Program, Arkansas State University, State University, Jonesboro, AR 72467, USA*
[3] *Chemistry and Physics Program, Arkansas State University, State University, Jonesboro, AR 72467, USA*

Correspondence should be addressed to Robert Engelken; bdengens@astate.edu

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Properties of electrodeposited semiconductor thin films are dependent upon the electrolyte composition, plating time, and temperature as well as the current density and the nature of the substrate. In this study, the influence of the electrodeposition parameters such as deposition voltage, deposition time, composition of solution, and deposition temperature upon the properties of In_2S_3 films was analyzed by the Taguchi Method. According to Taguchi analysis, the interaction between deposition voltage and deposition time was significant. Deposition voltage had the largest impact upon the stoichiometry of In_2S_3 films and deposition temperature had the least impact. The stoichiometric ratios between sulfur and indium (S/In: 3/2) obtained from experiments performed with optimized electrodeposition parameters were in agreement with predicted values from the Taguchi Method. The experiments were carried out according to Taguchi orthogonal array $L_{27}(3^4)$ design of experiments (DOE). Approximately 600 nm thick In_2S_3 films were electrodeposited from an organic bath (ethylene glycol-based) containing indium chloride ($InCl_3$), sodium chloride (NaCl), and sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$), the latter used as an additional sulfur source along with elemental sulfur (S). An X-ray diffractometer (XRD), energy dispersive X-ray spectroscopy (EDS) unit, and scanning electron microscope (SEM) were, respectively, used to analyze the phases, elemental composition, and morphology of the electrodeposited In_2S_3 films.

1. Introduction

During the last few decades solar energy has received attention due to increased environmental concerns over traditional energy resources such as coal, oil, and natural gas. Fossil fuel prices will rise over time and resources may eventually deplete. Hence, the world's current electricity supply is facing government, businesses, and consumer pressures to support development of alternative energy resources such as solar cells. The solar industry has come of age lately and the world's most efficient solar cell from Sharp can convert an impressive 44.4% of incoming photon energy into electrical energy [1]. Prices of solar panels have continued to drop while the market size of the US solar industry grew 34% between 2011 ($8.6 billion, 1,187 MW) and 2013 ($11.5 billion, 3,317 MW) [2]. However, scientists continue to research novel semiconductor materials and deposition techniques that can provide higher efficiencies and low-cost solar panels with less environmental impact upon the Earth.

In this paper, we report studies on electrodeposition of In_2S_3, an environmentally friendly replacement to CdS for solar cell applications as a buffer layer. In_2S_3 films were electrodeposited onto molybdenum-coated glass substrates. Electrodeposition is a low-cost, nonvacuum, and large industrial scale-based deposition technique to deposit material efficiently and uniformly. However, the electrochemistry behind it is complex due to multiple deposition parameters that may have individually and in tandem an impact upon the properties of the material [3, 4]. The Taguchi Method was used to optimize electrodeposition parameters in order to improve the stoichiometry of In_2S_3 films, which is one of the most important properties of any photovoltaic material and critical to obtaining the desired band gap and performance. Therefore, in the present study, the primary goal was to improve the stoichiometry while avoiding nonuniformity and nonadherency in the electrodeposited In_2S_3 films. Taguchi analysis helped us to analyze the effect of each deposition parameter upon the stoichiometry of In_2S_3 films.

2. Materials and Methods

2.1. Indium Sulfide (In_2S_3). In_2S_3 is an important member of III–VI group of midgap semiconducting sulfides, applicable for optoelectronics, solar cells, and photoelectric devices [2]. In_2S_3 is an indirect band gap semiconductor with potential to become a nontoxic alternative to CdS as a buffer layer in copper indium gallium selenide/sulfide- (CIGS-) based solar cells [5, 6]. It is a promising buffer material for photovoltaic applications because of its stability, reasonably wide band gap (2.3 eV) [7, 8], and photoconductive behavior [9]. Several reports have been published on deposition of In_2S_3 by different deposition techniques (both wet and dry), in thin film and powder form, with diverse morphologies [7, 10, 11]. In CIGS-based solar cells buffered with In_2S_3, efficiencies of 15.7% [12] have been achieved, which is slightly less than the 16% efficiency reported for CdS-based solar cells deposited by chemical bath deposition (CBD) [13]. Electrodeposited In_2S_3-buffered CIGSe solar cells have yielded 10.2% efficiency [14]. However, the use of ethylene glycol as an organic electrolyte for the electrochemical synthesis of In_2S_3 films has not been reported previously, with the exception of IEEE conference proceedings [3] regarding our work at the Optoelectronic Materials Research Laboratory (OMRL), Arkansas State University, Jonesboro, AR.

2.2. Electrodeposition. Electrodeposition is widely used in the coating industry and is considered to be a low-cost technique for large surface coatings with full coverage and high growth yield [15]. It was introduced by Kröger in the field of semiconductors in 1978, while working on cathodic deposition of CdTe, an absorber material [16]. Since then, electrodeposition has emerged as a method for the synthesis of semiconductor thin films and manufacturing of nanostructures such as chalcogenides [17]. Electrodeposition takes place when voltage is applied across the electrodes (anode and cathode) immersed in an electrolyte. The anode is anodized and the cations in the solution start moving towards the cathode with the help of the electric field created in the electrochemical cell. The reduction reaction takes place at the surface of the cathode and leads to deposition of the desired material. The process provides high material transfer/utilization efficiency, *in situ* measurements [18], precision control with proper bath chemistry, and environmental safety in terms of solvent emissions [14]. However, most of the work on semiconductor electrodeposition is limited to a few technologically important semiconductors. There are several deposition parameters which can affect the properties of the semiconductor material [19]. Many fundamental aspects of the electrodeposition of semiconductors are still misunderstood and not clearly defined. Since In_2S_3 shows promise and has not been studied as extensively as some semiconductors, in this work we determine the optimal deposition parameters for the electrodeposition of In_2S_3 thin films to obtain proper stoichiometry, crystalline structure, and morphology.

2.3. Taguchi Method. The "Taguchi Method" is a powerful tool developed by Genichi Taguchi in 1966 to improve the quality of industrially manufactured products [20]. It is a simple and effective technique that aims to optimize manufacturing processes in order to obtain the optimal performance. Today, this statistical tool is frequently applied to engineering, pharmaceutical, and biotechnology industries [21, 22].

Taguchi believed that this robust design could help to minimize (if not eliminate) a loss of quality which ultimately results in cost to society [23]. He defined the sensitivity (signal-to-noise ratio, *S/N*) as the logarithmic function for the response analysis (the characteristic performance that could be "stoichiometry" as it is in our case) of chosen deposition parameters to generate optimal design [22]. This analysis helps to compare the performance of a product with changing *S/N* ratios depending upon experimental procedures. The *S/N* ratio can integrate with the Taguchi orthogonal array (TOA) design of experiments and predict values (optimal) to achieve improved performance in the product and the process [21]. It is a suitable method to statistically analyze thin films since there are so many electrodeposition parameters that may have an impact upon the properties of semiconductor thin films. In the past, the Taguchi Method has been applied to various thin films ($CuInSe_2$, TiN, and Ni) [21–24]. Figure 1 depicts the flowchart of the steps involved in the Taguchi Method.

2.4. Steps

(1) Select Characteristic Performance. The initial step in the Taguchi Method involves selecting a characteristic performance that is affected by different parameters in the manufacturing process. The stoichiometric ratio between sulfur and indium was chosen as a characteristic performance in this study. The Taguchi Method will allow investigating how different parameters affect the means and variances of the stoichiometry of In_2S_3 films. Furthermore, this will help improve the functioning of the process and quality of the product.

(2) Select Deposition Parameters and Their Levels. Based upon the preliminary experiments and results, deposition parameters significantly affecting the stoichiometry of In_2S_3 films were selected. These deposition parameters include voltage, time, composition of solution, and temperature at three different levels, as specified in Table 1. The values of the levels were changed to study the effects of individual deposition parameters, as well as their interactions, upon the responses, with the least number of experimental runs.

The levels for each deposition parameter were chosen such as to cover the combinations where optimal conditions could potentially exist.

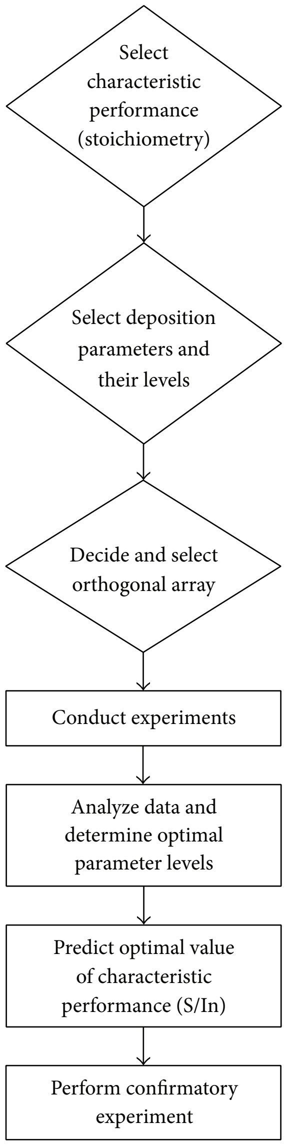


Figure 1: Steps in the Taguchi Method for design of experiments.

(3) Select Orthogonal Array Taguchi Design of Experiments (DOE). Taguchi orthogonal array L_{27} (3^4) design of experiments (DOE) (see Table 2) was applied to identify the critical deposition parameters. An orthogonal array of L_{27} was selected for conducting experiments at three levels for four deposition parameters, as mentioned above. In Table 2, Columns 1, 2, 5, and 9 represent deposition parameters A, B, C, and D. The design speeds up the process of experimentation and additionally saves time and resources.

(4) Conduct Experiments. According to L_{27} DOE, there are a total of 27 experiments needed to complete this study. For each experiment, three trials were performed to gain balance in the DOE and achieve high accuracy in the data. Hence, a total number of **81** experiments were performed.

(5) Analyze Data and Determine Optimal Parameter Levels. With the Taguchi Method, the analysis consisted of analysis of means (ANOM) and analysis of variance (ANOVA) for *S/N* ratios. The effect of each deposition parameter at a given level upon the quality of In_2S_3 films can be best estimated using ANOM. The basic goal of ANOVA is to estimate the variance in the film quality, owing to the deposition parameters in terms of *S/N* ratios.

A main effect plot for *S/N* ratios helped us to determine the optimal value for each deposition parameter.

(6) Predict Optimal Values: Orthogonal Regression Analysis. Orthogonal regression analysis helped improve the mean characteristic performance value and drive it closer to the target value, thus improving the quality of the product. It narrows down the scope of the manufacturing process and identifies the problem with the help of data already in existence.

(7) Perform Confirmatory Experiment. The final step in the Taguchi Method involves the validation of experiment and results from optimal deposition parameters to acquire the targeted value of the characteristic performance, that is, the stoichiometric ratio between sulfur and indium.

3. Experimental Details

A three-electrode electrochemical cell (see Figure 2) containing an ethylene glycol (organic solvent) bath of sulfur S (precipitated, 99.5%), sodium thiosulfate $Na_2S_2O_3{\cdot}5H_2O$ (99+%), indium chloride $InCl_3$ (anhydrous, 99.99%, metal basis), and sodium chloride NaCl (metal basis, 99.99%) from Alfa Aesar was used to conduct experiments with three different compositions as shown in Table 1.

A Ag/AgCl reference electrode from Fisher Scientific filled with potassium chloride (KCl) and ethylene glycol ($C_2H_6O_2$), a Mo-coated glass substrate (Mo sputtered onto 0.12-inch thick soda lime glass, 1 inch × 1 inch) as the working electrode (cathode), and graphite (1.25 inch × 1.25 inch) as a counter electrode (anode) were used to perform experiments. A digital potentiostat (WaveNow) from Pine Research Instrument Company was used for supplying voltage. A digital hotplate from Fisher Scientific (Isotemp 11-400-49SHP) was used to heat and stir the solution. Magnetic agitation of the organic bath was produced with a commercial Teflon-coated magnetic stir bar centered at the bottom of the glass beaker. The stir rate was kept constant at 300 rpm.

Molybdenum-coated glass substrates were cleaned in an acetone solution in an ultrasonic bath (Cole-Parmer 8890) and vibrated for 15 min. The organic electrolytic solution was prepared by dissolving elemental S in 150 mL of ethylene glycol and heating the solution at 150°C. Once the S was fully dissolved, the solution was cooled to 80°C, and then $InCl_3$ (0.05 M) and NaCl (0.1 M) were added. $Na_2S_2O_3{\cdot}5H_2O$ (used as an additional source for sulfur) was then added. The solution was continuously stirred and uniformly heated to avoid precipitation of sulfur in the cell and aging of the In_2S_3 colloid (small size chemical traces/species that stand idle at the walls or bottom of the beaker) formed by trace reduction and chemical precipitation of the solutes. The solution was then used for electroplating In_2S_3 onto the substrate. In_2S_3films were first slowly cooled to room

Table 1: Control deposition parameters and levels for the electrodeposition of In_2S_3 thin films.

Level	"A," deposition voltage (V)	"B," deposition time (min)	"C," composition of solution	"D," deposition temperature (°C)
1	−0.6	3	0.1 M S + 0.05 M $InCl_3$ + 0.1 M NaCl	150
2	−0.7	6	0.1 M S + 0.1 M $Na_2S_2O_3 \cdot 5H_2O$ + 0.05 M $InCl_3$ + 0.1 M NaCl	160
3	−0.8	9	0.2 M S + 0.05 M $InCl_3$ + 0.1 M NaCl	170

Table 2: Taguchi orthogonal array L_{27} (3^4) design of experiments with interactions.

Exp. number	1 (A)	2 (B)	3 ($A \times B$)	4 ($A \times B$)	5 (C)	6 ($A \times C$)	7 ($A \times C$)	8 ($B \times C$)	9 (D)	10	11 ($B \times C$)	12	13
1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	2	2	2	2	2	2	2	2	2
3	1	1	1	1	3	3	3	3	3	3	3	3	3
4	1	2	2	2	1	1	1	2	2	2	3	3	3
5	1	2	2	2	2	2	2	3	3	3	1	1	1
6	1	2	2	2	3	3	3	1	1	1	2	2	2
7	1	3	3	3	1	1	1	3	3	3	2	2	2
8	1	3	3	3	2	2	2	1	1	1	3	3	3
9	1	3	3	3	3	3	3	2	2	2	1	1	1
10	2	1	2	3	1	2	3	1	2	3	1	2	3
11	2	1	2	3	2	3	1	2	3	1	2	3	1
12	2	1	2	3	3	1	2	3	1	2	3	1	2
13	2	2	3	1	1	2	3	2	3	1	3	1	2
14	2	2	3	1	2	3	1	3	1	2	1	2	3
15	2	2	3	1	3	1	2	1	2	3	2	3	1
16	2	3	1	2	1	2	3	3	1	2	2	3	1
17	2	3	1	2	2	3	1	1	2	3	3	1	2
18	2	3	1	2	3	1	2	2	3	1	1	2	3
19	3	1	3	2	1	3	2	1	3	2	1	3	2
20	3	1	3	2	2	1	3	2	1	3	2	1	3
21	3	1	3	2	3	2	1	3	2	1	3	2	1
22	3	2	1	3	1	3	2	2	1	3	3	2	1
23	3	2	1	3	2	1	3	3	2	1	1	3	2
24	3	2	1	3	3	2	1	1	3	2	2	1	3
25	3	3	2	1	1	3	2	3	2	1	2	1	3
26	3	3	2	1	2	1	3	1	3	2	3	2	1
27	3	3	2	1	3	2	1	2	1	3	1	3	2

temperature to avoid thermal shock by immersing in warmed ethylene glycol and then rinsed with distilled water and acetone. The samples were stored in airtight plastic boxes.

4. Results and Discussions

4.1. Energy Dispersive X-Ray Spectroscopy (EDS). After conducting all 81 experiments, the elemental compositions for the electrodeposited In_2S_3 films were determined using EDS on the scanning electron microscope (SEM) from Tescan (Model VEGA TS 5136 XM). The INCA X-Sight (Model 7378) from Oxford Instruments is integrated with the SEM for EDS to function. The films were scratched off of the Mo-coated glass substrates because sulfur peaks (K lines) in EDS overlap with molybdenum peaks (L lines) from the substrates during acquisition at about 2.3 keV.

Following removal, the film was collected on an aluminum stub in powder form with the help of adhesive tabs. EDS was performed on three different areas over the surface distribution of the scratched-In_2S_3 film collected on the stub to calculate the mean S/In molar ratio for each film (see Figure 3 and Table 3). The In_2S_3 films may contain oxygen, carbon, aluminum, and molybdenum, as is evident from Table 3 (see Spectra 1 and 2). The In_2S_3 films may oxidize

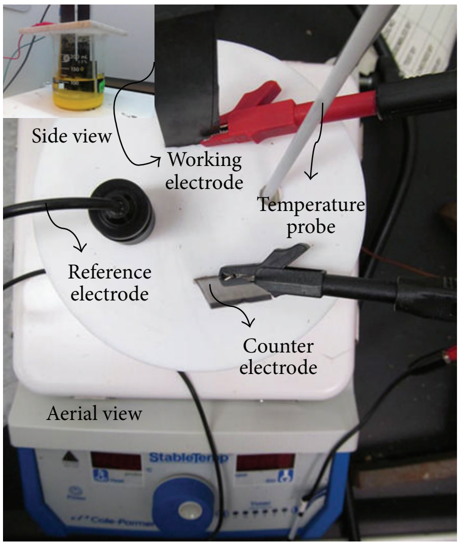


FIGURE 2: Three-electrode electrochemical cell.

TABLE 3: EDS analysis (Experiment Number 5, Trial 2).

Spectrum	Atomic %						
	O	C	S	Mo	Al	In	S/In
Spectrum 1	16.7	21.27	37.41	0	0	24.62	1.519
Spectrum 2	1.05	20	44.45	3.21	0	31.29	1.421
Spectrum 3	0	0	60.32	0	0	39.68	1.520
Mean	5.91	13.75	47.39	1.07	0	31.86	**1.487**

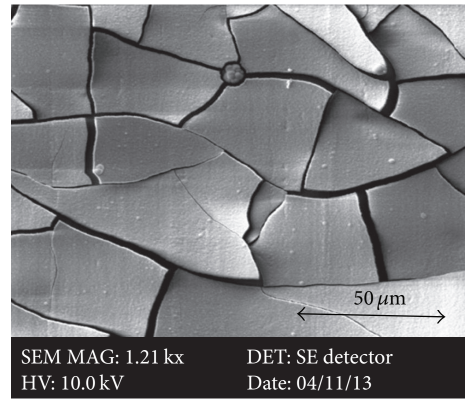
over a period of time, especially if not properly/immediately stored. Since the adhesive on the aluminum stub used to collect the scratched-In_2S_3 film contains carbon, EDS may detect carbon and also aluminum, as a part of the composition of the film. Molybdenum may also be detected by EDS as films were scratched off of the molybdenum-coated glass substrate. However, the stoichiometric ratios between sulfur and indium were close to optimal values, which is also evident from Table 3.

Hence, the S/In ratio calculated for each experiment was the mean of the mean S/In ratios determined from all three trials for the same experiment. The S/In ratios determined for all 27 experiments are listed in Table 4.

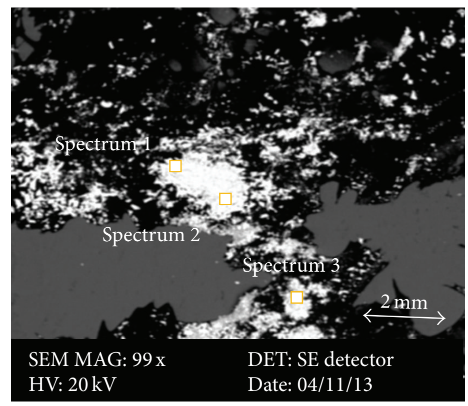
4.2. Signal-to-Noise Ratio (S/N) Analysis. Signal-to-noise ratio (S/N) was calculated using Minitab 16 in response to these stoichiometric ratios to measure the quality characteristic. The average S/N ratio was an average of all S/N ratios of a deposition parameter at a given level.

The formula used to calculate the S/N ratio is given by the following equation ("y" is the mean value of the performance characteristic for a given experiment and "s" is the variance):

$$S/N = 10 \log \frac{\overline{y}_i^2}{s_i^2}, \tag{1}$$



(a)



(b)

FIGURE 3: E5,2 (Experiment Number 5 and Trial Number 2): (a) SEM image of In_2S_3 film at 1.21 kX. (b) SEM image of scratched off film on an aluminum stub at 99 X with selected surface area (squares) for EDS analysis.

where

$$s_i^2 = \frac{1}{N_i - 1} \sum_{u=1}^{N_i} \left(y_{i,u} - \overline{y}_i \right) \tag{2}$$

$$\overline{y}_i = \frac{1}{N_i} \sum_{u=1}^{N_i} y_{i,u}, \tag{3}$$

where i is the experiment number, u is the trial number, and N_i is the number of trials for experiment i.

Using the above mathematical expressions, S/N ratios response for each deposition parameter and its level were calculated and are given in Table 5.

The response table includes ranks based upon delta statistics (▲), which compare the relative magnitude of effects for each deposition parameter. The symbol ▲ is the highest average S/N ratio for each parameter minus the lowest average S/N ratio for the same (e.g., in case of parameter "A," ▲ = 34.79 − 23.21 = 11.58). Ranks are assigned based on ▲ values; Rank 1 is assigned to the highest ▲ value, Rank 2 to the second highest ▲ value, and so on. Therefore, deposition voltage had the most significant impact upon the stoichiometry of the In_2S_3 films, and deposition temperature

Table 4: Sulfur to indium (S/In) molar ratios from EDS.

Uniformity	L_{27} orthogonal array experiment	S/In molar ratio
■	1	1.1556
■	2	1.2567
■	3	1.2313
■	4	1.3697
■	5	1.3132
■	6	1.3196
■	7	1.6671
■	8	1.4445
■	9	1.4097
■	10	1.2559
■	11	1.3510
■	12	1.3297
■	13	1.3818
□	14	1.3910
□	15	1.4462
□	16	1.3684
□	17	1.4012
□	18	1.46
□	19	1.2894
□	20	1.2354
□	21	1.4032
□	22	1.3520
□	23	1.2807
□	24	1.4150
□	25	1.4108
□	26	1.2442
□	27	1.4221

■ Uniform In_2S_3 films.
□ Nonuniform In_2S_3 films.

Table 5: Response table for signal-to-noise ratios.

Levels	*A*, deposition voltage (V)	*B*, deposition time (min)	*C*, composition of solution	*D*, deposition temperature (°C)
1	34.79	31.61	24.68	25.04
2	23.21	25.73	30.92	30.13
3	23.63	24.52	26.15	27.18
▲	11.58	7.08	6.23	5.10
Rank	1	2	3	4

had the least significant impact. The corresponding main effects and interaction plots between the parameters are also shown in Figures 4 and 5, respectively.

In the main effects plot, if the line (represents the grand mean of *S/N* ratios with respect to response) for a particular deposition parameter is nearly horizontal, the parameter has no significant effect. The highest average *S/N* ratio defines the optimal level (encircled) for that deposition parameter. Therefore, the optimal deposition parameters for the electrodeposition of In_2S_3 films are A1, B1, C2, and D2. On the other hand, a deposition parameter for which the line has the largest slope has the most significant effect. It is clear from the main effects plot that deposition parameter A (deposition voltage) was the most significant parameter while parameter D (deposition temperature) was the least significant. In the interaction plots, if the lines are nonparallel, then there is an interaction between parameters and if the lines cross, strong interaction occurs. From Figure 5, it can be seen that there is a strong interaction between parameters A and B, and there is a moderate interaction between parameters A and C and A and D.

4.3. Orthogonal Regression Analysis. Orthogonal regression equations were formulated for estimating predicted values to improve stoichiometry over a specified range of deposition voltage, the most significant factor of all, as shown in Figure 6. The In_2S_3 films deposited with these predicted values produced uniform In_2S_3 thin films with an average S/In molar ratio of 1.493 (see Table 6).

Confirmatory experiments with optimal and predicted values (from the main effect plot for *S/N* ratios and the orthogonal regression plot) from Taguchi analysis were repeatedly performed to verify stoichiometric ratios between sulfur and indium. The In_2S_3 films were grown at −0.685 V for 3 min in a bath containing 0.1 M each of sulfur and sodium thiosulfate, at a deposition temperature of 160°C. The films were uniform and adherent. The stoichiometric ratios between sulfur and indium from these experiments were in agreement with predicted values from the Taguchi Method. The S/In molar ratio was calculated to be 1.49, almost equal to the ideal S/In molar ratio of 3/2. Table 6 shows the EDS data for one of the confirmatory experiments. The electrodeposited In_2S_3 films produced from these experiments were approximately 600 nm thick. The thickness of the films was measured using a surface profilometer from Veeco (Dektak Model 6M).

However, the In_2S_3films exhibited narrow cracks within 1 μm width (see Figure 3(a)).

4.4. X-Ray Diffraction. An X-ray diffractometer from the Rigaku Corporation (Model D/MAX-B System) was used for phase identification of the crystalline structure of the electrodeposited In_2S_3 films synthesized at optimal values before and after heat treatment. Figure 7 shows the XRD plot of an as-grown and then annealed In_2S_3 film. The film was annealed in air for 2 hours at 250°C. It is evident from the figure that the as-grown In_2S_3 films exhibited a beta-phase crystalline structure. The In_2S_3 peaks were slightly more narrow and intense for annealed films, which indicated that the grains were better crystallized.

5. Conclusion

In_2S_3 films with nearly ideal stoichiometric ratios were successfully electrodeposited onto Mo-coated glass from an organic bath. The optimized electrodeposition parameters obtained by the Taguchi Method were as follows: deposition

TABLE 6: EDS data for In_2S_3 films grown at optimal values obtained by the Taguchi Method (confirmatory results).

Spectrum	Atomic %						
	O	Si	S	Mo	In	Total	S/In
Spectrum 1	6.54	0.0	54.1	3.12	36.2	100.0	1.493
Spectrum 2	0.00	0.0	56.6	8.36	37.5	100.0	1.51
Spectrum 3	0.00	0.0	55.1	7.27	37.5	100.0	1.471
Spectrum 4	14.4	0.0	50.6	2.82	33.7	100.0	1.5
Spectrum 5	0.00	0.0	58.3	0.00	40.5	100.0	1.443
Spectrum 6	0.00	0.0	59.8	0.00	39.9	100.0	1.498
Spectrum 7	4.21	0.0	57.4	0.00	38.3	100.0	1.501
Spectrum 8	0.00	0.0	60.2	0.1	39.7	100.0	1.53
Mean	3.14	0.0	56.5	2.7	37.9	100.0	**1.493**
Max.	14.4	0.0	60.2	8.36	40.5		
Min.	0.00	0.0	50.6	0.00	33.7		

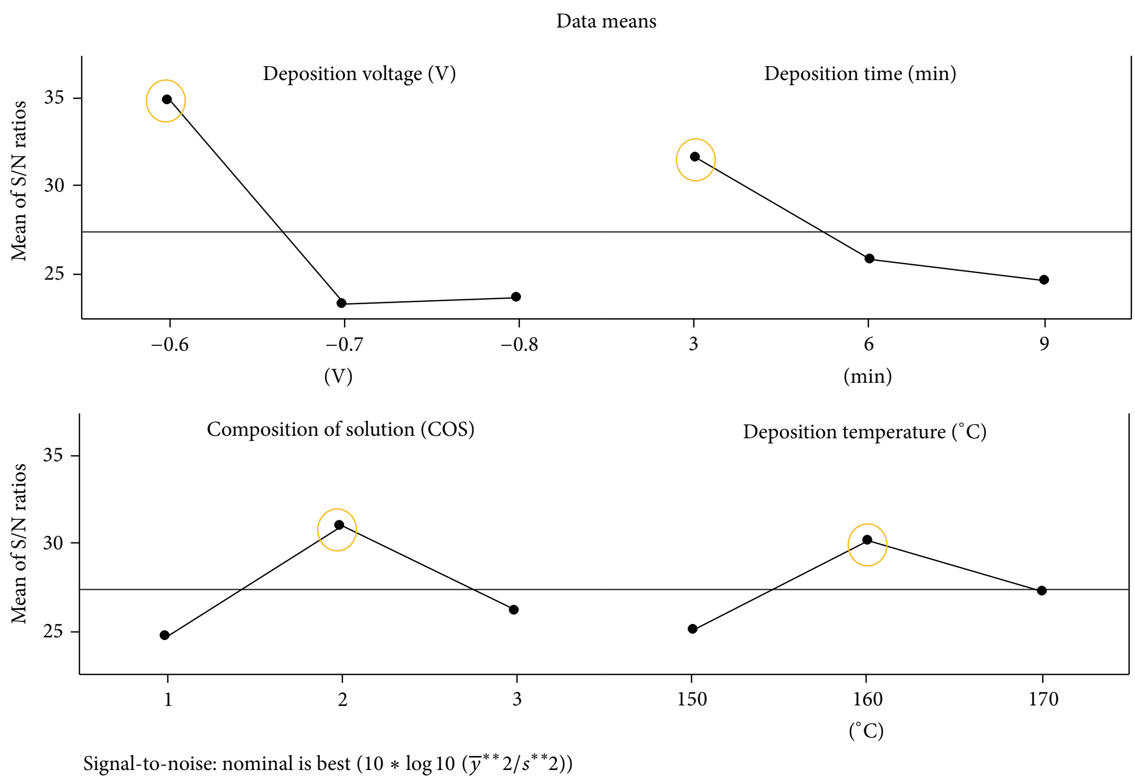


FIGURE 4: Main effect plot for S/N ratios.

voltage, −0.6 V; deposition time, 3 min; composition of solution, 0.1 M S + 0.1 M $Na_2S_2O_3{\cdot}5H_2O$ + 0.1 M NaCl + 0.05 M $InCl_3$; and deposition temperature, 160°C. The ANOVA analysis for means and S/N ratios showed that deposition voltage had the largest impact upon the stoichiometry of the In_2S_3 films, and deposition temperature had the least significant impact. Also deposition voltage and deposition time showed stronger interaction (largest impact upon the characteristic performance) between them compared to other deposition factors. Furthermore, orthogonal regression analysis produced plots with a predicted value for deposition voltage (−0.685 V). From the EDS analysis, it was clear that In_2S_3 films exhibited nearly ideal stoichiometric molar ratios between sulfur and indium. The S/In molar ratio calculated was 1.49, almost equivalent to the ideal S/In molar ratio of 3/2. XRD plots revealed that electrodeposited films exhibit β-In_2S_3 crystalline structures. The In_2S_3 films were uniform and adherent with approximately 600 nm thickness. Eventually,

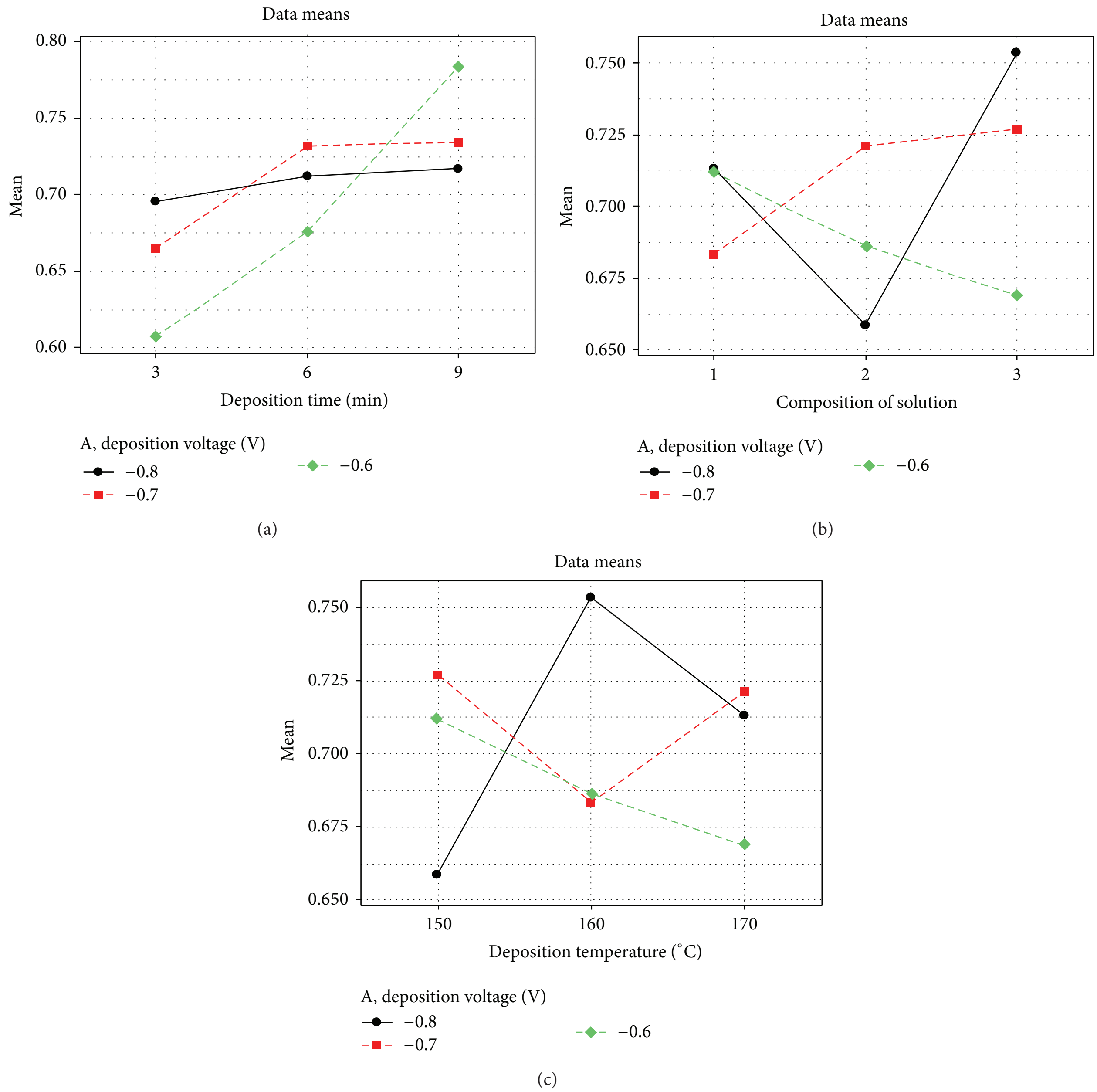


FIGURE 5: Interaction plot for deposition voltage versus (a) deposition time, (b) composition of solution, and (c) deposition temperature.

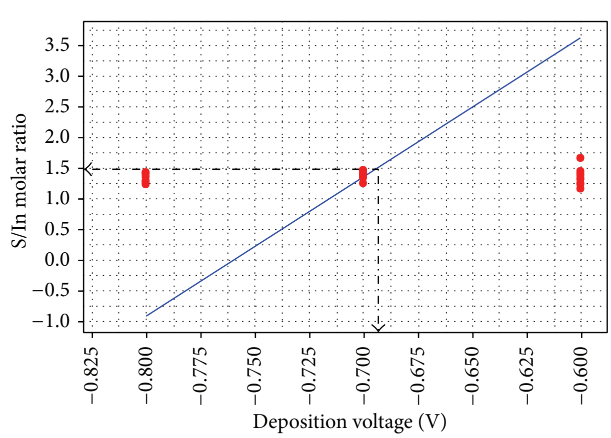


FIGURE 6: Orthogonal regression plot of S/In molar ratio versus deposition voltage with fitted line.

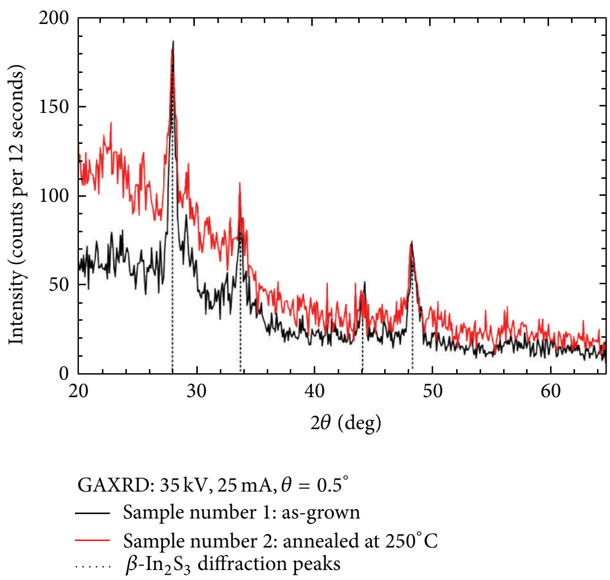


Figure 7: Glancing angle X-ray diffraction spectra for as-grown and annealed (in air at 250°C) In_2S_3 film.

In_2S_3 films will be combined with electrodeposited $CuInS_2$ or CdTe films to form heterojunction solar cells.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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