Statistical Analysis of Electroplated Indium (III) Sulfide (In_2S_3) Films, a Potential Buffer Material for PV (Heterojunction Solar Cells) Systems, using Organic Electrolytes

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ABSTRACT

In_2S_3 has received attention as an alternative to CdS as the buffer layer in heterojunction solar cells. Although having a bandgap of 2.0 eV relative to 2.5 eV for CdS, the lower toxicity and environmental impact of indium relative to cadmium, and significant photosensitivity, compel ongoing research [1]. Indium sulfide thin films were deposited onto molybdenum-coated glass (SiO_2) substrates by electrodeposition from organic baths (ethylene glycol-based) containing indium chloride (*$InCl_3$*), sodium chloride (*NaCl*), and sodium thiosulfate (*$Na_2S_2O_3.5H_2O$*), the latter used as an additional sulfur source along with elemental sulfur (*S*). The Taguchi method was used to optimize the deposition paramters so as to minimize non-uniformity, cracks, and improper stoichiometry. The measured performance characteristics (molar ratio (In:S) and crack density) for all of the In_2S_3 films were calculated to analyze the effect of each deposition factor (deposition voltage, deposition temperature, composition of solution, and deposition time) involved in the electrodeposition process by calculating the sensitivity (signal to noise, *S/N*, ratios).

Keywords: In_2S_3, Taguchi method, electrodeposition, solar cell, thin film

1 INTRODUCTION

In_2S_3 is an important member of III-VI group midgap semiconducting sulfides, applicable for optoelectronics, solar cells, and photoelectric devices [2]. Scientists have been involved in conducting investigations for last few years now to study novel materials with enhanced material properties. After intensive research efforts they have yielded fundamental understanding that In_2S_3 can be a non-toxic alternative to CdS in copper indium gallium selenide/sulfide (CIGS)-based solar cells [3], [4]. In_2S_3 is a promising buffer material for photovoltaic applications because of its stability, wider bandgap, and photoconductive behavior [5]. It has good photoluminescence properties [6], [7]. Several reports have been published on deposition of In_2S_3 thin films by different deposition techniques (both wet and dry), both in thin film and powder form, with diverse morphologies [5]. In In_2S_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) [8]. Electrodeposited In_2S_3-based CIGSe solar cells have yielded 10.2% efficiency [9].

Electrodeposition is considered to be a low-cost technique for applying thin films on a substrate with full coverage and high growth yield [10]. It provides high material transfer/utilization efficiency, precision control with proper bath chemistry, and environmental safety in terms of solvent emissions [9]. However, there are several deposition parameters which can affect the properties of In_2S_3 thin films. Therefore, it is important to determine the optimal deposition parameters for the electrodeposition of In_2S_3 thin films to obtain proper stoichiometry, crystalline structure, and morphology.

In this paper, we present studies on electrodeposition of In_2S_3 films onto molybdenum-coated glass. The Taguchi method was used to obtain optimal deposition parameters based upon the data obtained from scanning electron microscopy (SEM), digital image (from SEM) analysis, and energy dispersive X-ray spectroscopy (EDS). The goal was to avoid non-uniformity, cracks, and improper stoichiometry. The statistical analysis helped us to analyze the effect of each deposition factor on the stoichiometry and the morphology of In_2S_3 films.

2 TAGUCHI METHOD

The "Taguchi method" are statistical methods developed by Genichi Taguchi to optimize the procedure and improve the quality of industrially manufactured products. These methods are frequently applied to engineering, pharmaceutical, and biotechnology industries today [11].

The Taguchi method was developed in 1954 to bring improvements in the quality of a product. Taguchi believed that this robust design can help to minimize (if not eliminate) the loss of quality which results in an ultimate cost to society [12]. He defined the sensitivity (signal-to-noise ratio, S/N) for the response analysis (characteristic performance) of selected physical quantities. This analysis helps to compare the performance of a product with changing S/N ratios depending upon procedures (in our case deposition parameters and their levels). The S/N ratio can combine with the Taguchi orthogonal array for the design of experiments and predict values(optimal) to achieve improved performance in the product and the process [11].

It is a very suitable method to statistically analyze the study of thin film coatings, because there are so many deposition parameters involved in electrodeposition that could have an impact on the properties of In_2S_3 thin films. In the past, the Taguchi method has been applied to various thin film ($CuInSe_2$, TiN, Ni) coatings synthesized by different deposition methods [11], [12], [13].

3 EXPERIMENTAL DETAILS

The electrodeposition was carried out in a three-electrode cell configuration using an organic bath of S (precipitated, 99.5%), $Na_2S_2O_3.5H_2O$ (pentahydrate, 99+ %), $InCl_3$ (anhydrous, 99.99 %, metal basis), and NaCl (Puratronic®, 99.999%, metal basis) with three different compositions. Ethylene glycol was used as a solvent. Based upon preliminary results, a range of optimal electrodeposition parameters (factors and their levels): deposition voltage, deposition temperature, composition of solution, and deposition time, were selected.

A three electrode-cell was used for all the experiments in this work. A Ag/AgCl reference electrode from Fisher Scientific filled with KCl and $C_2H_2O_6$, a Mo-coated glass substrate (Mo sputtered onto 0.12-inch thick silicon glass; 1 inch x 1 inch) as the working electrode (cathode), and graphite (1.25 inch x 1.25 inch) as a counter electrode (anode) were used. A digital potentiostat (WaveNow) from Pine Research Instrumentation was used for supplying electrode potential and for cyclic voltammetry. A digital stirring 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 in the bottom of the glass beaker to achieve laminar rotations. The stir rate was kept constant at 300 rpm.

Molybdenum-coated glass substrates were cleaned in an acetone solution in an ultrasonic bath (Branson 2510) and vibrated for 5 min. The organic electrolytic solution was prepared by dissolving elemental S in 150 ml of ethylene glycol by heating the solution at 150°C. Once the S was fully dissolved, the solution was cooled down to 80°C, and then $InCl_3$ (0.05 M), and NaCl (0.1 M) were added to solution. $Na_2S_2O_3.5H_2O$ (used as an additional source for sulfur) was added to solution after $InCl_3$ and NaCl were dissolved. The solution was continuously stirred to avoid aging of the colloid and the precipitation of sulfur in the cell. The solution was then used for electroplating In_2S_3. After deposition, In_2S_3 films were slowly cooled down to room temperature by dipping in ethylene glycol, and then rinsed with distilled water and acetone. All the samples were stored in an airtight plastic box.

3.1 Taguchi Design of Experiments (DOE)

For the present work, an orthogonal array of L_{27} was selected for conducting experiments at three levels for four factors, as shown in Table 1. The levels for each deposition factor were chosen such as to cover practically all the combinations where optimal conditions could potentially exist. According to orthogonal array L_{27}, there were a total of 27 experiments needed for this study. For each experiment, three trials were performed to achieve high accuracy in the data. Hence, a total number of 81 experiments were performed. With the Taguchi method, the analyses consisted of analysis of mean (ANOM) and analysis of variance (ANOVA) for S/N ratios. The effect of each control factor at a given level on the quality of In_2S_3 film can be best estimated using ANOM. The basic goal of ANOVA is to estimate the variance in the film quality, owing to the control factor in terms of S/N ratios.

Level	Deposition Voltage (V)	Deposition Time (min)	Composition of Solution	Deposition Temperature (°C)
1	-0.6	3	0.1M S + 0.05M $InCl_3$ + 0.1M NaCl	150
2	-0.7	6	0.1M S + 0.1M $Na_2S_2O_3.5H_2O$ +0.05 M $InCl_3$ + 0.1M NaCl	160
3	-0.8	9	0.2M S + 0.05 M $InCl_3$ + 0.1M NaCl	170

Table 1: Control Factors and Levels for the Electrodeposition of In_2S_3 Thin Films

In the past, our electrodeposited In_2S_3 films have shown good stoichiometries but poor morphologies. Films are usually non-uniform and thicker around the edges, and sometimes flake away into the solution when pulled out from the cell. The films have shown cracks which could possibly result in loss of charged carriers and insufficient electrical transport within the solar cell. Therefore, for this study, the measured performance characteristic (or object function) were selected to be crack density (number/87.36 µm square) and molar ratio (In:S) to avoid those issues. To study the crack behavior as a function of deposition parameters, digital analysis of SEM images was performed using a fracture and buckling analysis program. This program has been written using MATLAB Version 7.1 (R14). It investigates and detects the dark features of the image compare 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 to the SEM image, where this line pattern is perpendicular to cracks. The intersection between the analysis lines and cracks are determined [14]. Hence, the crack density is determined by dividing the number of intersections with the commulative line length, as shown in Fig.1(a). Hence, SEM images were taken for all 81 In_2S_3 films to calculate crack density. Similarly, molar ratio (S/In) was determined for all 81 films using EDS. Ideally 60% S and 40% In yield a stoichiometric ratio (S/In) of 3/2. The EDS pattern for Experiment No. 2 (Trial 1) is shown in Fig. 1 (b), verifying that the film contains S and In.

4 RESULTS AND DISCUSSION

The cracked morphology of electrochemically deposited In_2S_3 thin films have been reported previously by several scientists, for instance in [15], [16], and [17]. The reason is still not fully known. In our study, we found that the deposition voltage and deposition time are, respectively, the most and second-most significant deposition factors in terms of eliminating cracks and obtaining proper stoichiometry, and that deposition temperature is the least significant. The interaction between the factors, deposition voltage and deposition time, is also significant, compared to other factors. These results are visualized using Minitab's (Version 16) mean effect plot for means, as shown in Fig. 2 (a). This plot is used in conjunction with ANOVA and DOE to examine differences among level means for one or more factors. The optimal values obtained from the plot for four deposition factors are encircled. The points in the plot are the mean of the response variables (crack density and S/In molar ratio) at the various levels of each factor, with a reference line drawn at the grand mean of the response data. Further, orthogonal regression equations are formulated for estimating predicted values of crack density and stoichiometry over a specifed range of deposition voltage, the most significant factor of all, as shown in Fig. 2 (b) and (c). The films deposited with these predicted values produced uniform In_2S_3 thin films with planar-surface morphology, and S/In ratio of 59/41.

In our study, we observed that the In_2S_3 films tend to start cracking from the edge of the substrate. As the deposition voltage/time increases, those cracks tend to propagate into the middle part of the substrate causing the film to eventually flake and fall into the solution. The films grown at higher (-0.8 V) negative potential yielded In- rich films.

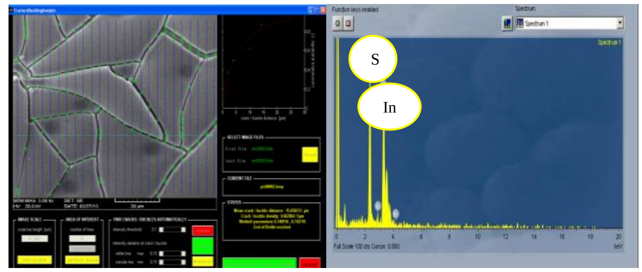

Figure 1: (a) Fracture and Buckling Analysis Program, (b) EDS Pattern of the In_2S_3 Film from Experiment No. 2.

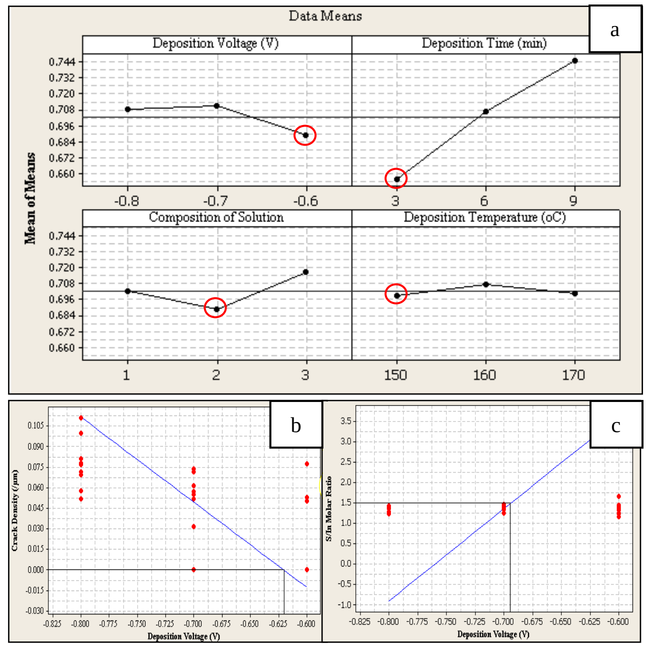

Figure 2: (a) Mean Effect Plot for Means (Crack Density and S/In Molar Ratio), (b) Orthogonal Regression Plot of Crack Density (number/87.36 µm square) vs. Deposition Voltage with Fitted Line, and (c) Orthogonal Regression Plot of Molar Ratio vs. Deposition Voltage (S/In) with Fitted Line.

5 CONCLUSION

In_2S_3 films with good stoichiometric ratios and planar surface morphologies have been successfully deposited onto Mo-coated glass from an organic bath by electrodeposition. The optimized deposition parameters obtained from Taguchi analysis were as follows: deposition voltage, -0.6 V; deposition time, 3 min; composition of solution, 0.1 M S + 0.1 M $Na_2S_2O_3.5H_2O$; and deposition temperature, 150 ^oC. ANOVA analysis for means and S/N ratios showed that deposition voltage has the largest impact on the stoichiometry and crack density of the films, and that deposition temperature has the least significant impact. Also deposition voltage and deposition time together showed stronger interaction (largest impact on the performance characteristic) between them compared to other deposition factors. Furthermore, the orthogonal regression analysis produced plots which predicted values for deposition voltage to achieve desired characteristic performance. These predicted values were as follows: -0.69 V for achieving proper S/In ratio and -0.62 V for achieving films with non-crack morphology.

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