Electrodeposited SnS thin films from aqueous solution

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AbstractSnS film has been produced by electrodeposition technique onto ITO (indium-tin-oxide) coated glasssubstrates using acid solution containing SnCl₂, Na₂S₂O₃and EDTA. electrodepositionwas carried out at 20°C. Prior to the deposition, a cyclic voltammetry experiment was carried out between two potential limits (+1000 to -1300 mV versus SCE) to probe the effect of the applied potential and to determine the most likely suitable electrodeposition potential for the deposition of tin sulfide.

Keywords: Solar cells; thin films; EDTA; electrodeposition.

I. INTRODUCTION

Photovoltaics are universally recognized to be one of the alternative renewable energy sources supplement power generation using conventional fuels [1-4]. Tin monosulphide (SnS) as a novel "absorber" layer in the fabrication of thinfilm hetero-junction solar cells has attracted more attention in recent years [5-7]. SnS has an optical absorption coefficient of around 10^5 cm⁻¹ above the fundamental absorption edge, which is higher than GaAs and CdTe. Its indirect band gap and direct band gap are estimated to be around 1.0-1.3 eV and 1.38 eV, which is near the optimum value of 1.4 eV to absorb the spectrum of solar radiation most efficiently in single junction solar cells [8, 9]. Its constituent elements Sn and S are abundant in nature and less toxic than many other solar cell elements or compounds. In theory, the conversion efficiency of the solar cell fabricated with SnS thin films can be up to 25% [10].

In this work, we deposit SnS by electrochemical deposition. Electrodeposition (ECD) is the cheapest method available to deposit thin films because of several advantages, such as the possibility for large-scale production, minimum waste of components, and easy monitoring of the deposition process [7,9,11,12]. The presence of complexing agents in the solution during the electrodeposition process of metal chalcogenide thin films is extremely important [13]. The potential benefits of additives include: brightening the deposit, increasing the grain size, changing mechanical and physical properties, reducing

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stress, reducing pitting, and increasing the lifetime ofdeposition bath as well as the adhesion of the deposited film on the substrate [14].

II. EXPERIMENTAL

The electrodeposition bath was prepared from tin anhydrous $SnCl_2$, sodium thiosulphate ($Na_2S_2O_3$) and disodium ethylenediaminetetra-acetic acid (EDTA) salts. The complexing agent was used to obtain the Sn-EDTA solution. The pH was adjusted to around 1–1.6 using HCl.The pH was maintained low to prevent the formation of hydroxyl and insoluble compounds. The solution was continuously deaerated with N_2 during electrodeposition.

An EG&PARC 273A Potentiostat/Galvanostat coupled with computer under "power suite software" was used to control the electrodeposition process and to monitor the current and voltage profiles. The electrodes were immersed in the electrodeposition bath containing stannous chloride (SnCl₂.2H₂O), sodium thiosulphate (Na₂S₂O₃.5H₂O) and ethylene di-amine tetra-acetic (EDTA). The electrolyte was prepared using analytical grade reagents and deionizer distilled water. In every single run, the electrolyte was stirred well to homogenize the viscous, gelatinous mass.

EDTA was used to chelate with Sn^{+2} to obtain a Sn-EDTA complex (reaction.1). Nitrogen gas was flowed into the solutions prior to mixing to remove any dissolved O₂. Hydrochloric acid (HCl) is added to pH 1.6 to prevent the formation of hydroxyl species and insoluble compounds. The depositions were carried out at room temperature by varying the deposition potential to determine the optimal conditions of deposition of tin-sulfide thin films.

$$Sn^{2+} + EDTA \leftrightarrow Sn(EDTA)^{2+}(1)$$

In reaction (1), the stability of $Sn(EDTA)^{2+}$ chelate is determined by the concentration of Sn^{2+} , EDTA, and $Sn(EDTA)^{2+}$, and pH value of the solution. The stability

constant is usually used to characterize the chelating effect of EDTA (reaction.2).

$$K_{Sn(EDTA)^{2+}} = \frac{c_{Sn(EDTA)^{2+}}}{c_{Sn^{2+}}c_{EDTA}}$$
(2)

Here C_{Sn2+} , C_{EDTA} and $C_{Sn(EDTA)2+}$ are the concentration of Sn^{2+} , EDTA and $Sn_{(EDTA)2+}$, respectively. $K_{Sn(EDTA)2+}$ is the stability constant. The acidity of the bath affects not only chelating effect of EDTA but also the existent form of Sn^{2+} . Therefore, EDTA can be used to control Sn deposition rate [15-19].

III. RESULTS AND DISCUSSION

Cyclic voltammograms in the mixture of tin chloride, sodium thiosulfate and EDTA electrolyte

Figure.1 compares the cyclic voltammograms of ITO working electrode in the mixture of $SnCl_2$ and $Na_2S_2O_3$ in solutions without (fig.1.a) and with (fig.1.b) 0.01M EDTA respectively.



Figure1: Cyclic voltammograms of 0.01M $SnCl_2+ 0.01M$ Na₂S₂O₃+0.01M KCl (a) and 0.01M $SnCl_2+0.01M$ Na₂S₂O₃+0.01M EDTA+ 0.01M KCl (b) on ITO substrate at 20°C. Scan rate 20mV in pH =1.2

From the figure, a reduction wave can be observed at around -0.9 V (fig.1.a) and -1 V (fig.1.b) versus SCE, which is due to the simultaneous reduction of SnCl₂ and Na₂S₂O₃ corresponded to the formation of SnS (reaction.3) layer onto the ITO working electrode. The anodic peak around -0.26 V versus SCE corresponded to the stripping of deposited layers in the reverse scan.

$$Sn^{2+} + S^{2-} \to SnS \tag{3}$$

The voltammograms (fig.1(a-b)) show a crossover between cathodic current branch which is characteristic of the nucleation and growth process [17,19]. The cyclic voltammogram showed the curve as a flick out during the reverse scan. This phenomenon indicated that nucleation of tin sulfate occurs at a surface of substrate in the system.

From the data obtained through CV, we can conclude with the addition of EDTA, it is easier to co-deposit Sn an S and obtain stoichiometric SnS thin films favorably. The deposition potential can ascertained to be more negative than -0.70V versus SCE.

IV. CONCLUSION

The polycrystalline SnS thin films can be electrodeposited on the ITO substrate in the presence of EDTA as a complexing agent. The optimal deposition potential to deposit SnS thin films between -0.70 and -1 V versus SCE. These preliminary results about the preparation and performance of the thin films made were very encouraging.

ACKNOWLEDGMENTS

The authors would like to thank the laboratory (LAIGM) and the Department of Process Engineering for the provision of chemical products.

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