INFLUENCE OF THE DEPOSITION TIME ON THE STRUCTURE AND
MORPHOLOGY OF THE ZnS THIN FILMS ELECTRODEPOSITED ON
INDIUM TIN OXIDE SUBSTRATES

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Zinc sulphide thin films were grown on indium tin oxide glass substrates by
electrodeposition method in an aqueous solution that contained zinc chloride, sodium
thiosulfate and triethanolamine. Effect of deposition time on the deposition of ZnS thin
films was investigated. The crystallinity and surface morphology of ZnS thin films were
studied by X-ray diffraction and atomic force microscopy, respectively. From the X-ray
diffraction results, it could be seen that the prominent growth orientation was (200) plane.
The number of peaks related to ZnS increased as the deposition time was increased from
15 to 30 min. However, the total ZnS peaks reduced to two peaks as the deposition time
was further increased to 60 min. Based on the atomic force microscopy analysis, it was
found that the grain size, thickness and surface roughness were strongly influenced by
deposition time.

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1. Introduction

Intensive research has been performed in the past to study the deposition and
characterization of semiconducting metal chalcogenide thin films. Zinc sulphide is an important II-
VI semiconductor with a wide band gap which is suitable for applications in solar cells, solar
selective decorative coatings, UV light emitting diode, photocatalysis and phosphors in flat panel
displays. ZnS thin films have been grown by various methods including chemical bath deposition
[1], atomic layer epitaxy [2], RF reactive sputtering [3], pulsed-laser deposition [4] and
electrodeposition method [5]. Electrodeposition method is a perspective competitor in thin films
preparation due to many advantages such as the possibility for large-scale production, minimum
waste of components and easy monitoring of the deposition process. Several chalcogenides have
been electrodeposited such as As2S3 [6], CdSe [7], ZnSe [8], CuInSe2 [9], CuInTe2 [10] and
Cu4SnS4 [11].

In this paper, we report for the first time the cathodic electrodeposition for the synthesis of
ZnS thin films from aqueous solution using zinc chloride, sodium thiosulfate and triethanolamine
at a constant potential of -1.1 V versus SCE, 45 °C and pH 3. The effect of deposition time (15, 30
and 60 min) on the properties of thin films has been investigated in order to better understand the
growth conditions. The structure and morphology of ZnS thin films were analyzed by X-ray
diffraction and atomic force microscopy, respectively.
2. Experimental

2.1 Preparation of thin films

All the chemicals used for the deposition were analytical grade reagents and all the solutions were prepared in deionised water (Alpha-Q Millipore). The zinc sulphide thin films were prepared from an acidic bath using aqueous solutions of zinc chloride (0.01 M) and sodium thiosulfate (0.05 M) acted as a source of Zn\(^{2+}\) and S\(^{2-}\) ions, respectively. The concentrated triethanolamine solution was used as complexing agent to chelate with Zn\(^{2+}\) to obtain Zn-TEA complex solution. The EG&G Princeton Applied Research potentiostat driven by a software model 270 Electrochemical Analysis System was used for the zinc sulphide electrodeposition in a three-electrode cell. The cell consisted of indium doped tin oxide (ITO) glass substrate as working electrode, platinum wire as counter electrode and saturated calomel electrode (SCE) as reference electrode, separately. Before deposition, the glass substrate was degreased with ethanol for 10 min. Then, ultrasonically cleaned with distilled water for another 10 min and dried in desiccator. Purified nitrogen was flowed into the deposition bath for few minutes to create oxygen free environment. The pH was adjusted to 3 by using hydrochloric acid under the control of a pH meter. The zinc sulphide thin films were prepared at various deposition periods (15, 30 and 60 min) at -1.1 V versus SCE at 45 °C. After the deposition, the thin films were washed with distilled water and kept for analysis.

2.2 Characterization of thin films

The structure of the thin films was monitored by X-ray diffraction (XRD) with a Philips PM 11730 diffractometer equipped with a CuK\(_\alpha\) (\(\lambda=0.15418\) nm) radiation source. Data were collected by step scanning from 20° to 60° with a step size of 0.05° (2\(\theta\)). The surface morphology, thickness and roughness were examined by recording atomic force microscopy images with a Q-Scope 250 in contact mode with a commercial Si3N4 cantilever. Values of root mean square (RMS) roughness were calculated from the height values in the atomic force microscopy images using the commercial software.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of ZnS thin films deposited on indium tin oxide glass substrates at various deposition periods. For the films prepare at shorter period (15 min), the XRD pattern shows the presence of single peak at 2\(\theta\)=33.3°. However, the number of peaks referred to ZnS increased to three peaks as the deposition time is increased to 30 min. The (111), (200) and (220) diffraction peaks are observed as shown in Fig. 1b. The presence of sharp peaks is an indication of the polycrystalline nature of the thin films. These peaks are coincident with the JCPDS data of cubic phase of ZnS. Comparison of observed d-spacing values with standard d-spacing values confirms that electrodeposited films show cubic structure of ZnS[12] (Reference code: 00-065-0309). The lattice parameter is found to be a=b=c=5.4 Å. We have observed that the intensities of ZnS peaks increase at this deposition period, indicating a better crystallinity. When the deposition time is increased from 15 to 30 min, the thickness of ZnS thin films increases and the crystallinity is improved. This observation is also supported by the results obtained from AFM. The films deposited at longer period (60 min) show diffraction peaks at 2\(\theta\)=28.9° and 33.3° which correspond to the (111) and (200) planes. The intensities of the (111) and (200) peaks show a noticeable decrease while the (220) plane disappear as compared with the films deposited for 30 min. Overall, based on the XRD patterns, we find that the (200) peak is stronger compared to other peaks. Huang et al. [5] had reported the cubic ZnS thin films with oriental growth along (200) direction could be obtained using electrodeposition method.
Fig. 1. X-ray diffraction patterns of ZnS thin films deposited at different deposition periods
(a) 15 min (b) 30 min (c) 60 min ZnS; In$_{1.875}$O$_{3}$Sn$_{0.125}$.

Fig. 2. 2-dimensional (a) and 3-dimensional (b) atomic force microscopy images of ZnS thin films deposited for 15 min.
On the other hand, the presence of the indium tin oxide [13] (JCPDS reference No.: 01-089-4597) peaks in the XRD patterns is due to the ITO glass substrates used during deposition. Owing to the penetration depth of the X-ray beam, peaks from the ITO substrate are present in all samples. These diffraction peaks at $2\theta = 30.5^\circ$, $35.5^\circ$, $50.8^\circ$ and $54.4^\circ$ can be indexed to (222), (400), (440) and (600), respectively.

![Image of XRD patterns](image)

**Fig. 3.** 2-dimesional (a) and 3-dimensional (b) atomic force microscopy images of ZnS thin films deposited for 30 min

It is well known that the atomic force microscopy (AFM) is one of the effective ways for the surface analysis due to its high resolution and powerful analysis software. Fig. 2(a), Fig. 3(a) and Fig. 4(a) show the two-dimensional while Fig. 2(b), Fig. 3(b) and Fig. 4(b) display three-dimensional AFM images of ZnS films deposited for 15, 30 and 60 min, respectively and the scan area is 20 $\mu$m x 20 $\mu$m. It can be seen from the AFM image that ZnS films prepared for 15 min produce the smoothest surface (6 nm). These films have the smallest grain size (0.4 $\mu$m) and the density of the films is very high. Meanwhile, the films deposited for 30 min have the largest grain size (1 $\mu$m) and produce the roughest surface morphology (288 nm) than other thin films. As the deposition time is further increased to 60 min, the grain size grows small (0.6 $\mu$m) as shown in Fig. 4(a) and Fig. (b). Hence, the films will become smoother (26 nm) than that deposited for 30 min.
On the other hand, the thickness of the films was studied using AFM images. At the right side of the images, an intensity strip is shown, which indicates the depth and height along the z-axis. The film thickness increased from 128 to 2025 nm as the deposition time is increased from 15 to 30 min, then, decreased to 220 nm as the deposition time is further increased to 60 min. The AFM results illustrate that the deposition time significantly affect the grain size, film thickness and surface roughness of ZnS thin films.

4. Conclusions

Cathodic electrodeposition in the presence of triethanolamine as complexing agent was used to prepare zinc sulphide thin films on indium tin oxide substrates. From the X-ray measurement results, it could be seen that the prominent growth orientation was (200) plane. The number of peaks referred to ZnS increased as the deposition time was increased from 15 to 30 min. However, the total ZnS peaks reduced to two peaks as the deposition time was further increased to 60 min. Based on AFM results, the surface roughness, film thickness and grain size could be well
controlled by deposition time during the deposition. We concluded that deposition for 30 min at 45 °C was the best condition to prepare good quality ZnS thin films under the current conditions.

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References