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ARAŞTIRMA MAKALESİ /**RESEARCH ARTICLE**

# INFLUENCE OF PH ON THE STRUCTURAL AND MORPHOLOGICAL PROPERTIES OF ZnS THIN FILMS

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## *ABSTRACT*

The ZnS thin films have been obtained from aqueous solution by means of cyclic voltammetry method. The electrochemical bath consisted of zinc sulphate, sodium thiosulfate and triethanolamine. The effect of electrolyte pH on the properties of ZnS thin films was investigated within the range from 3 to 9. The cyclic voltammetry was used to analyse the electrochemical bath. The structural and morphological of thin films were investigated by X-ray diffraction and atomic force microscopy, respectively. The thin films obtained have cubic structure and single phase as analysed by XRD. As the pH was reduced from 9 to 3, the intensities of the peaks corresponding to ZnS increased. AFM image shows the thin films prepared at pH 3 are homogeneous and well covered on the substrate. These thin films consist of small grains which lead to deposition of smoother films. However, as the pH increases up to 7, the number of grains decreases and larger grain size could be obtained. Therefore, the pH plays a major role in synthesis of ZnS thin film and the pH 3 is the best pH under current conditions.

**Keywords:** Cyclic Voltammetry, Thin films, Zinc sulphide, Metal chalcogenide.

# ZnS ÇİNKO SÜLFÜR İNCE FİLMLERİN YAPIASAL VE MORFOLOJİK ÖZELLİKLERİNE PH ETKİSİ

## *ÖZ*

ZnS ince filmler çevrimsel voltametri yöntemiyle sulu çözeltiden elde edilmiştir. Elektrokimyasal banyo çinko sülfat, sodyum tiosulfat ve triethnalomine içermiştir. ZnS yapısal özellikleri üzerine elktrolitin pH etkisi 3-9 aralıklar arasında incelenmiştir. Çevrimsel voltametri elektro-kimyasal banyoyu analiz etmek için kullanılmıştır. Atomik kuvvet mikroskopu ve X-ışınları (XRD) kırınımı analizleri ile ince filmler yapısal ve morfolojik olarak incelenmiştir. Zns yapılar kübik yapıda ve tek fazlı olduğu XRD sonuçlarından elde edilmiştir. pH değeri 9'dan 3' e indirgendiğinde ZnS pik şiddetlerinin azaldığı gözlenmiştir. pH 3'de hazırlanan örneklerin kuvvet mikroskopu analizleri bu filmlerin alttaş ile uyumlu olarak büyüdüğü gösterilmiştir. Bu ince filmler bundan başka küçük tane büyüklüğüne sahip oldukları bu çalışmada gösterilmiştir. Diğer taraftan banyonun pH değeri 7'ye kadar arttırıldığına tane sayısı azalmış ve fakat tane büyüklüğü artmıştır. Böylece pH 3 değerindeki banyolamanın ince film hazırlamada önemli bir etkisi olduğu bu çalışma ile gösterilmiştir.

**Anahtar Kelimeler:** Çevrimsel voltmetri, İnce film, Zinc sülfür, Metal kalgonide

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# 1. INTRODUCTION

The preparation and characterization of metal chalcogenide of different groups have attracted considerable attention due to their brilliant applications. Zinc sulphide is an important II-VI compound semiconductor material with a wide direct band gap, abundance in nature and absence of toxicity. ZnS has been studied due to its wide applications such as photovoltaic devices, UV light emitting diode, photocatalysis and phosphors in flat panel displays. A variety of preparation techniques such as atomic layer epitaxy (Ihanus et al., 1997), thermal evaporation (Wu et al., 2008), pulsed laser deposition (McLaughlin et al., 1993), vacuum evaporation (Kumar et al., 2006), spray pyrolysis (Yazici et al., 2003), chemical bath deposition (Zhou et al., 2009) and electrodeposition (Huang et al., 2008) have been reported so far to obtain ZnS thin films.

Chemical bath deposition method is a simple method, which attractive features are the cost effectiveness, large scale production, low temperature growth and easily to set-up. Chemical bath deposition method is based on the reaction between dissolved zinc ions and sulphur-containing organic compound (sodium thiosulfate) in aqueous solution. The triethanolamine was used as complexing agents for depositing ZnS thin films. The complexing agent as a component of the chemical bath eliminates spontaneous precipitation by slowing down the release of the metallic ions on dissociation thereby resulting in slow precipitation of the compound. The preparations of various thin films using chemical bath deposition technique such as CuS (Ezema et al., 2006), CdS (Moualkia et al., 2009), $As_2S_3$ (Mane et al., 2004), $Cd_{0.5}Zn_{0.5}Se$ (Kale et al., 2007) and $Cu_4SnS_4$ (Anuar et al., 2009) have reported by several authors.

In the present study, we have demonstrated for the first time that it is feasible to synthesis ZnS thin film by means of cyclic voltammetry method at room temperature in the presence of triethanolamine. The influence of electrolyte pH on the film is studied. The cyclic voltammetry was used to analyse the electrochemical bath. Meanwhile, the deposited films were characterized by X-ray diffraction and atomic force microscopy for their structural and surface morphological studies.

# 2. EXPERIMENTAL

The electrochemical bath contained 0.05 M $ZnCl_2$ (25ml) and 0.05 M $Na_2S_2O_3$ (25 ml) along with concentrated triethanolamine (5 ml) which acted as a complexing agent. All these chemicals used were of analytical grades. The voltammetric study was performed using an Electrochemical Analyzer (BAS 100W, West Lafayette, Indiana, USA). The indium-doped tin oxide (ITO) glass was used as working electrode. The ITO glass was degreased with ethanol for 10 min, followed by distilled water rinse for 15 min in an ultrasonic bath. The saturated calomel electrode (SCE) and platinum wire were used as reference and counter electrodes, respectively. The pH of these electrolytes is within the range from 3 to 9. The pH was adjusted by addition of HCl solution. All electrolyte solutions were bubbled with nitrogen for 15 min. ZnS thin films were synthesized by cyclic voltammetry technique at room temperature. The deposition process was carried out from -300 to -1500 mV versus SCE at scan rate of 10 mV/s. After the deposition, the films were washed with distilled water and kept for analysis.

The structure of the film 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 25° 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 $Si_3N_4$ 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

Figure 1 shows the cyclic voltammograms obtained from solutions of zinc chloride, sodium thiosulfate and triethanolamine. The effect of electrolyte pH on the shape of voltammogram was investigated. In the forward scan, the cathodic current starts flowing at about -700 mV versus SCE for the film deposited at pH 3. This is due to the reduction of thiosulphate ions (Subramanian et al., 2001). Further studies revealed that the reduction of $Zn^{2+}$ ion in an acidic solution to Zn at -1000 mV (Riveros et al., 2002). We can conclude that the cathodic peak current increased markedly when the pH of electrolyte was reduced. It is clearly that in strongly acidic media (pH 3), the presence of a large concentration of $H^+$ which allow the rate of reduction of sodium thiosulfate to take place besides the hydrogen evolution. This indicated that strong dependency of the redox process on the pH of the electrolyte.

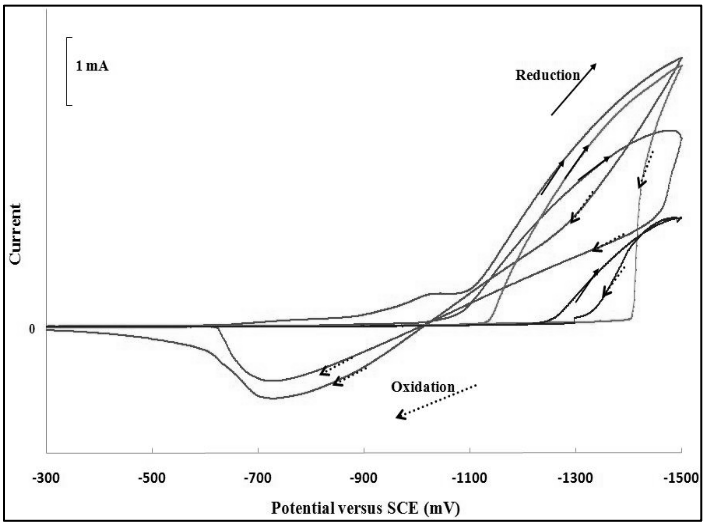


Figure1. Cyclic voltammograms recorded in electrochemical bath at different pH values

( ——— pH 3 ——— pH 5 ——— pH 7 ——— pH 9) contains 0.05 M zinc chloride, 0.05 M sodium thiosulfate and 5 ml of triethanolamine. Scan range in -300 to -1500 mV versus SCE and scan rate was 10 mV/s.

The structure and the phase of the samples have been examined by X-ray diffraction (XRD) method. In Figure 2, the XRD patterns for the samples deposited at different pH values are presented. The thin films obtained have cubic structure and single phase as analysed by XRD. The XRD pattern in Figure 2a corresponds to sample deposited at pH 3. The three peaks corresponding to (111), (200) and (220) planes were obtained. These peaks were identified by comparing the *d*-spacing values obtained from the XRD patterns with JCPDS (reference no.: 00-065-0309) data for ZnS (Dubrovin et al., 1983). The lattice parameters of the cubic structure are equal to a=b=c=5.4 Å. As the pH was increased from 5 to 9, the intensity of the peak corresponding to (200) plane decreased. This is accompanied by the disappearance of ZnS peak (220) as shown in Figure 2 (b-d). On the other hand, the XRD patterns also show that the intensities of indium tin oxide peaks were higher than the ZnS peaks for the films prepared at higher pH (pH 5-9). The presence of indium tin oxide (Nadaud et al., 1998) peaks (reference no.: 01-089-4597) comes from the substrates during deposition process. This indicates that a favourable condition to prepare ZnS thin film is pH 3. Therefore, these results point out that the pH has a great effect on the structure of the sample.

The atomic force microscopy (AFM) has been proved to be a convenient method to determine the grain size, thickness and surface morphology of a film. Figure 3 shows a three-dimensional AFM images (10x10 μm) of the ZnS thin films deposited at different pH values on the ITO substrate. The thin films prepared at pH 3 (Figure 3a) showed homogeneous and well covered on the substrate. These films consist of small grains (0.2 μm) which lead to deposition of smoother films (17 nm). As the pH increases up to 7, the number of grains decreases and larger grain size could be obtained (Figure 3b and 3c). The roughness values of 31 and 56 nm have been observed for samples prepared at pH 5 and 7, respectively (Table 1). Root mean square (RMS) roughness is defined as the standard deviation of the surface height profile from the average height, is the most commonly reported measurement of surface roughness (Jiang et al., 2005). The surface roughness of the film is unavoidable since grains were grown with different sizes and spherical in shapes. On the other hand, the fine grains were observed for the film prepared at pH 9. The grain size of the film was estimated to be 0.15 μm in diameter, which is much smaller than the grain size of the film prepared at pH 3. Therefore, the pH leads to change of the film morphology.

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. Table 1 shows the variation of film thickness with pH for ZnS thin films. From the data obtained, it is clear that the thickness of the film increased as the pH was increased up to 7. However, the films deposited at pH 9 produced thinner films compared to other pH values.

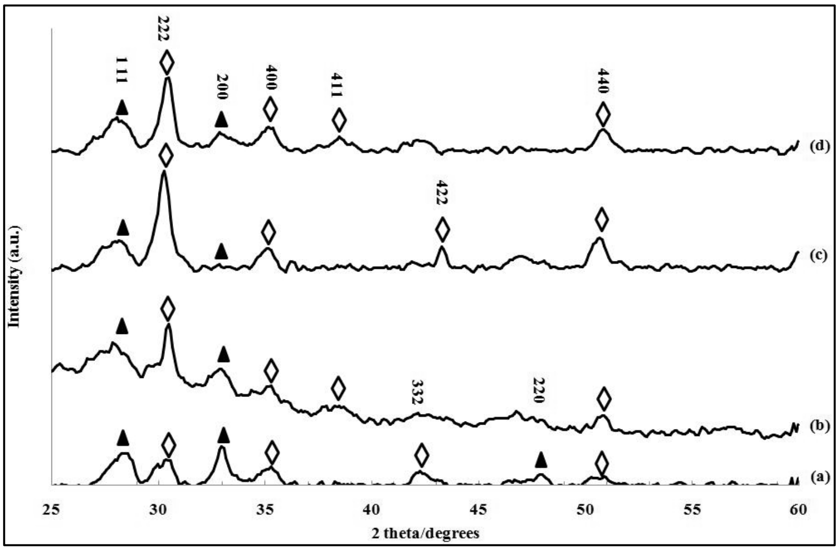


Figure 2. X-ray diffraction pattern of ZnS thin films deposited at different pH values (a) pH 3 (b) pH 5 (c) pH 7 (d) pH 9. ( ▲ ZnS; ◇ $In_{1.875}O_3Sn_{0.125}$ (ITO)

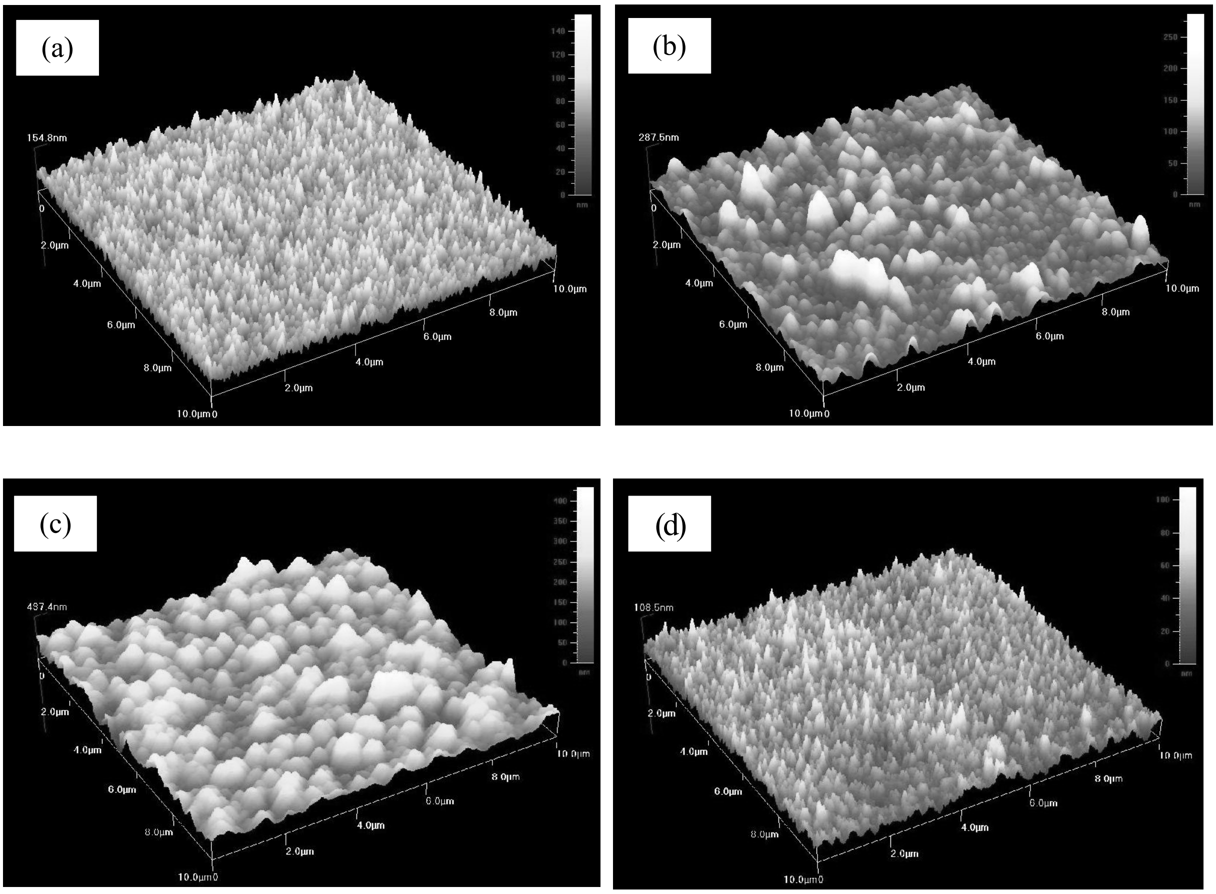


Figure 3. Atomic force microscopy images of ZnS thin films deposited at different pH values (a) pH 3 (b) pH 5 (c) pH 7 (d) pH 9.

Table 1. Thickness and surface roughness determined from atomic force microscopy for ZnS thin films prepared at different pH values

| pH | Root Mean Square of roughness (nm) | Thickness (nm) |
|---|---|---|
| 3 | 17 | 155 |
| 5 | 31 | 288 |
| 7 | 56 | 487 |
| 9 | 11 | 109 |

## 4. CONCLUSION

ZnS thin films were synthesized by cyclic voltammetry technique in room temperature. The thin films obtained have cubic structure and single phase as analysed by XRD. As the pH was reduced from 9 to 3, the intensities of the peaks corresponding to ZnS increased. AFM image shows the thin films prepared at pH 3 are homogeneous and well covered on the substrate. These thin films consist of small grains which lead to deposition of smoother films. However, as the pH increases up to 7, the number of grains decreases and larger grain size could be obtained. Therefore, the pH plays a major role in synthesis of ZnS thin film and the pH 3 is the best pH under current conditions.

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