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# Study on the Phase and Bath Electrochemical Properties in Electrodeposition of ZnS Film

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**ZnS does nearly not absorb sun light, it is the most suitable buffer layer material in solar cell. For preparing ZnS film with low cost, the bath electrochemical performance and the effect of deposition potential on the phase of ZnS films prepared by electrodeposition were studied under different electrodeposition conditions. The phases and morphology of product films were investigated by X-ray diffraction and scanning electron microscope respectively. Experimental results show that, it was more conducive to achieve co-deposition using the constant potential method. Compared with thiourea, it is easier to achieve co-deposition for ZnS. ZnS phase can be obtained under –1.0 ~ –1.6 V. When the deposition potential increased, the (100) crystal plane of the highest XRD peak of ZnS phase changed as (101) crystal plane. Well crystallized, dense and uniform ZnS film can be obtained under conditions of sodium citrate as complexing agent, sodium thiosulfate as sulfur source, ion ratio of Zinc and Sulfide 1 : 5 and –1.2 V.**

**Key words: ZnS, Electrodeposition, Deposition potential, Phase, Morphology.**

## Introduction

ZnS with sphalerite crystal structure is a compound semiconductor that belongs to II-VI group, has a direct transition type energy band with 3.5 ~ 3.7 eV band gap. Since ZnS does nearly not absorb sun light, it is the most suitable alternative for the buffer layer material CdS [1]. The methods for preparing ZnS thin films include chemical bath method [2-4], magnetron sputtering [5-7], spray pyrolysis [8], pulsed laser method [9] and electrical deposition [10, 11]. Chemical bath method was more widely applied among above methods. Most of these methods are not suitable for low-cost mass production due to detail experimental conditions and laboratory equipments. ZnS thin films prepared by chemical bath method contained $Zn(OH)_2$ and shows discontinuous surface [12]. Electrodeposition method has many advantages such as low cost and good system stability, can easily realize large-scale production [13]. It shows that phase formation of ZnS films was affected by many factors such as deposition potential, ion ratio, and complexing agent and bath pH [14]. In this work, for preparing ZnS film with low cost, the bath electrochemical performance and the effect of deposition potential on the phase of ZnS films prepared by electrodeposition were studied under different electrodeposition conditions with Zinc chloride, Sodium thiosulfate and complexing agent.

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## Materials and Methods

The solution consists of Zinc chloride, sodium thiosulfate and complexing agent with sodium citrate, sodium gluconate, ethylenediamine tetraacetic acid or ammonia. Three electrode devices consist of platinum electrode as auxiliary electrode, saturated calomel electrode as a reference electrode and tin oxide conductive glass substrate as a working electrode. The cyclic voltammetry curves were carried out on the PARSTAT 2273 electrochemical workstation produced by Princeton Applied Research Company with a scan rate of 10 mV/s and a range of −1~0 V. The phases of product samples were analyzed by X-ray diffraction (XRD) on the Bruker D8 Advance XRD system with Nifiltered Cu-Kα ($\lambda = 1.5059$ Å). The morphology of product films was observed using scanning electron microscope (SEM) with a model of JSM-6380LA made by Japan Electronics Co., Ltd.

## Results and Discussion

Our previous work has reported that, the plating solution with 30 mmol/L sodium citrate as the complexing agent was the best condition for electrodeposition of ZnS thin film [15]. In this experiment, the experimental variables are adjusted by controlling a single variable method.

### The effect of the sulfur source on the electrochemical performance of solution

Main compositions of the bath solution are shown in

**Table 1.** Main compositions of the bath solution.

| Main composition | Zinc chloride | Sulfur source: sodium thiosulfate, thiourea | Complexing agent: sodium citrate |
|---|---|---|---|
| Concentration | 15 mmol/L | 75 mmol/L | 30 mmol/L |

**Table 2.** The potential values of the solutions with different Sulfur sources.

| No. | Sulfur source | Oxidation peakpotential/ V | Reduction peak potential /V | Oxidation-reduction potential difference /V |
|---|---|---|---|---|
| 1 | sodium thiosulfate | -0.8638 | -1.4780 | 0.6141 |
| 2 | Thiourea | -0.8360 | -1.6201 | 0.7841 |

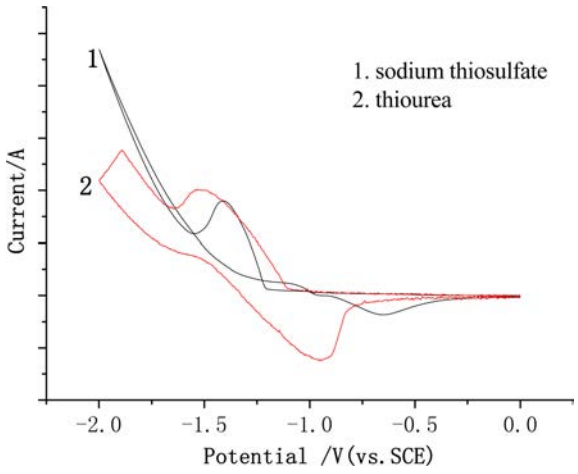


**Fig. 1.** Cyclic voltammetry curves of the solutions with different Sulfur sources.

table 1. Fig.1 shows the beginning reduction potential, reduction peak potential, even the oxidation and reduction peak potential of solution have changed when the sulfur source was different. The discharge potentials of both ions were closer; It was more conducive to achieve co-deposition using the constant potential method. As it can be seen from table 2, Compared with thiourea, when sodium sulfide is the sulfur source, the oxidation potential is negative and the redox potential difference is small, it is easier to achieve co-deposition for ZnS. So sodium sulfide was selected as sulfur source.

## The effect of Zinc and sulfide ions ratio on the electrochemical performance of solution

Fig. 2 shows the beginning of reduction potential, reduction peak potential, even the oxidation and reduction peak potential of solution have changed with the zinc and sulfide ratio changing. As it can be seen from table 3, with the increase of the sulfur ion ratio, the oxidation peak and reduction peak start to move toward the negative direction, then move to the positive direction at the ratio of 1 : 15. The horizontal distance

**Table 3.** The potential values of the solutions with different ion ratios of Zinc and Sulfide.

| No. | Concentration of sulfur source / mmol/L | Oxidation peak potential /V | Reduction peak potential /V | Oxidation-reduction potential difference /V |
|---|---|---|---|---|
| 1 | 15 | -0.8910 | -1.3910 | 0.5000 |
| 2 | 75 | -1.2257 | -1.5138 | 0. 2981 |
| 3 | 110 | -1.4276 | -1.7594 | 0.3318 |
| 4 | 150 | -1.4034 | -1.8042 | 0.4008 |
| 5 | 225 | -1.4005 | -1.8048 | 0.4043 |
| 6 | 300 | -0.6578 | -1.7735 | 1.1157 |

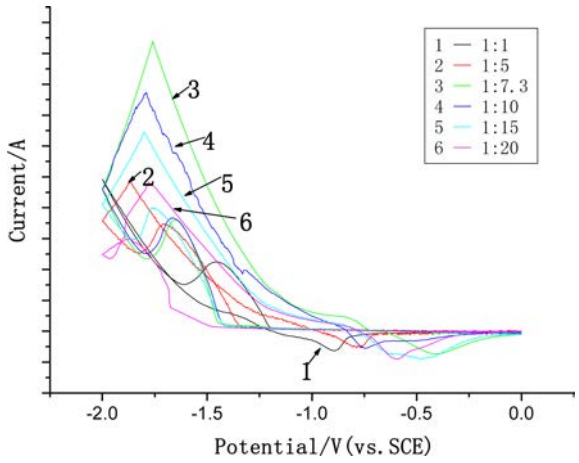


**Fig. 2.** Cyclic voltammetry curves of the solutions with different ion proportions of Zinc and Sulfide.

of oxidation peak and reduction peak first decreases and then increases, its reduction magnitude was very large when the zinc and sulfur ions ratio varied from 1:1 to 1:5. Starting from 1:5 as the zinc and sulfur ions ratio, the horizontal distance of oxidation peak and reduction peak begin to become larger. The zinc and sulfur ions ratio 1:5 was selected in later experiments, because it is easier to achieve co-deposition when the horizontal distance is small. So the range of the deposition potential was selected as −1.0 ~ −1.6 V.

## The effect of deposition potential on phase formation of ZnS films

Fig. 3 shows XRD patterns of the ZnS films under different deposition potentials by constant potential method under conditions of sodium citrate as complexing agent, sodium sulfide as sulfur source and zinc and sulfur ratio 1 : 5. The phase of target product ZnS on glass substrates can be obtained when the deposition potentials are −0.3 V, −0.5 V, −0.6 V and −0.8 V respectively. With the increase of the deposition potential, the XRD peak intensity ratio of ZnS changed, with the highest peak along (100) instead of (101) plane. There are XRD peaks for Sulfur when the deposition potential is −1.0 V and XRD peaks for zinc when the deposition potential is

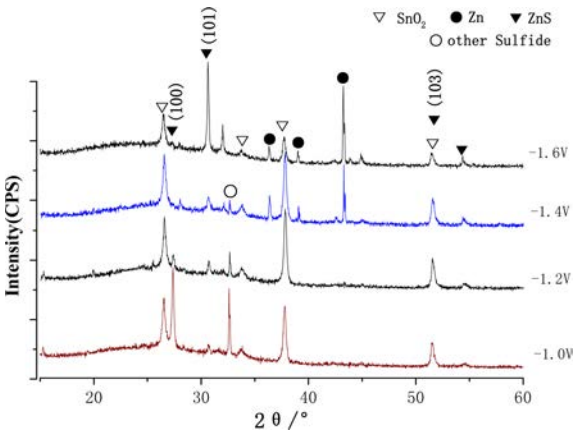


**Fig. 3.** XRD patterns of product films prepared under different deposition potentials.

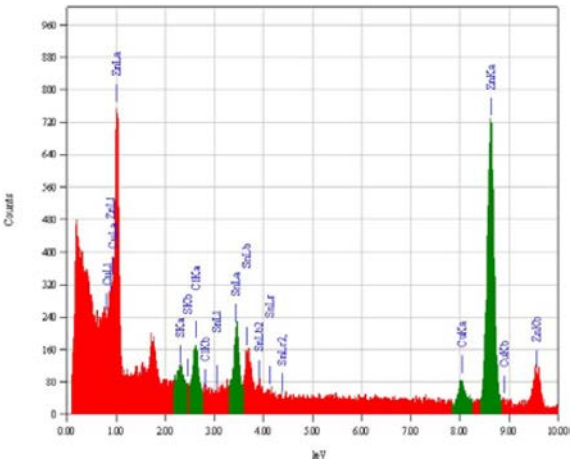

**Fig. 5.** The EDS image of ZnS films prepared under the potential-1.2 V.

−1.4 V. It demonstrates that the discharge rate of the zinc ion increased and the sulfur ion discharge rate decreases with the increase of deposition potential. The XRD results indicate that ZnS can be sythysized by electrodeposition, Zn and S atoms (ions) are obtained by electrochemical reaction and combined together.

## The morphology of ZnS film and composition analysis

Fig. 4 shows SEM images of ZnS films prepared under different deposition potentials. Combining Fig. 3 and Fig. 4, the phase and morphology of the product films are very different under different deposition potentials. The product film obtained under −1.0 V has relatively coarse particles, while the sample shows relatively small and uniform arrangement particles under −1.2 V. The uniformly and small particles were shown on the film obtained under −1.6 V. Fig. 5 gives the EDS image of ZnS films prepared under the potential −1.2 V. It indicates that the sample consits of Zn and S elements and other impurity elements contained in the substrates.

## Conclusions

ZnS phase in product films can be obtained under the deposition potentials of −1.0 ~ −1.6 V. The formation of ZnS process is electrodeposition, Zn and S atoms

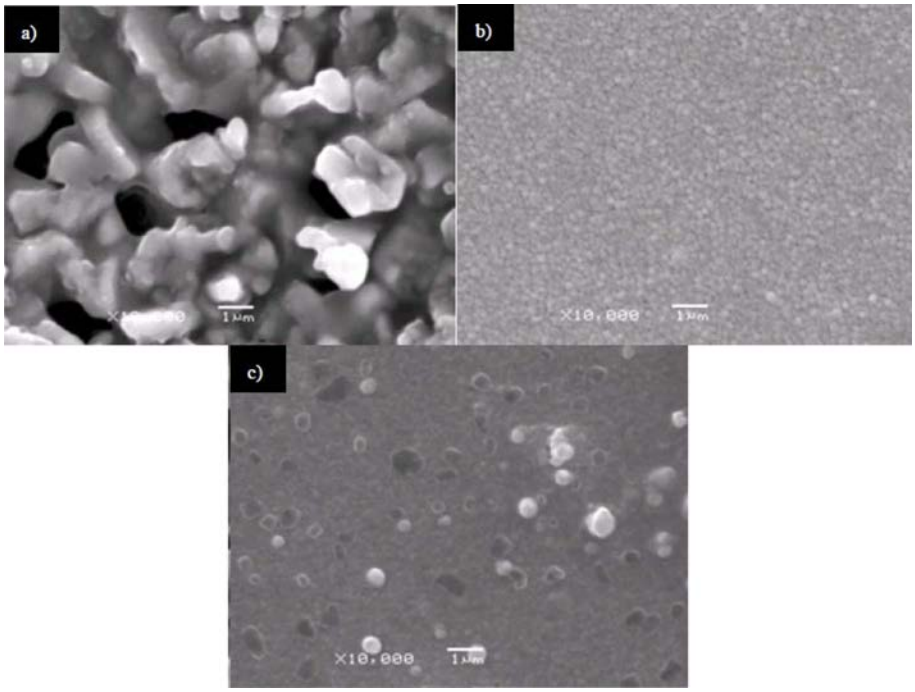


**Fig. 4.** SEM images of ZnS films prepared under different deposition potentials a) −1.0 V b) −1.2 V c) −1.6 V

(ions) are obtained by electrochemical reaction and combined together. When the deposition potential increased, the (100) crystal plane of the highest XRD peak of ZnS phase changed as (101) crystal plane. Well crystallized, dense and uniform ZnS film can be obtained under conditions of sodium citrate as complexing agent, sodium thiosulfate as sulfur source and the ion proportion of Zinc and Sulfide 1 : 5, −1.2 V.

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