



Chemical bath-deposited ZnS thin films: Preparation and characterization

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ABSTRACT

Chemical bath deposition of ZnS thin films from $\text{NH}_3/\text{SC}(\text{NH}_2)_2/\text{ZnSO}_4$ solutions has been studied. The effect of various process parameters on the growth and the film quality are presented. The influence on the growth rate of solution composition and the structural, optical properties of the ZnS thin films deposited by this method have been studied. The XRF analysis confirmed that volume of oxygen of the as-deposited film is very high. The XRD analysis of as-deposited films shows that the films are cubic ZnS structure. The XRD analysis of annealed films shows the annealed films are cubic ZnS and ZnO mixture structure. Those results confirmed that the as-deposited films have amorphous $\text{Zn}(\text{OH})_2$. SEM studies of the ZnS thin films grown on various growth phases show that ZnS film formed in the none-film phase is discontinuous. ZnS film formed in quasi-linear phase shows a compact and a granular structure with the grain size about 100 nm. There are adsorbed particles on films formed in the saturation phase. Transmission measurement shows that an optical transmittance is about 90% when the wavelength over 500 nm. The band gap (E_g) value of the deposited film is about 3.51 eV.

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1. Introduction

$\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$ (CIGS)-based thin-film solar cell efficiencies now exceed 19.5% (NREL group) [1] and progress in photovoltaics has a new manuscript with 19.9% has been reported [2]. These CIGS solar cells were typically fabricated using a cadmium sulfide (CdS) buffer layer in order to protect the junction region from sputtering damage during subsequent zinc oxide (ZnO) deposition and to modify the surface of CIGS absorber [3]. However, the quantum efficiency of a CdS/CIGS solar cell drops at short wavelengths due to optical absorption losses from the CdS layer. This implies that further improvement in the short circuit current (J_{sc}) can be achieved by replacing CdS with another appropriate wider band gap buffer material. In addition to these technical considerations, avoiding the use of cadmium compounds is desirable from the viewpoint of environmental safety.

One promising alternative material is ZnS thin film. Its band gap energy (E_g) of 3.68 eV at room temperature [4] makes it transparent to practically all wavelengths of the solar spectrum. In contrast CdS, with its band gap of 2.42 eV at room temperature [5], is highly absorbing for wavelengths below 520 nm [6]. There has been a considerable progress in using ZnS in CIGS thin-film solar cells, ZnO/ZnS/CIGS solar cells with efficiency of up to 18.6% have been fabricated [7].

A very attractive method for producing ZnS thin films, due to the possibility of large-area deposition at low cost is the so-called chemical bath deposition (CBD) method [8,9]. Ammonia and hydrazine are popular choices as the complexing agent in the CBD of ZnS thin films. For instance, Dona and Herrero [10] have deposited ZnS films using hydrazine hydrate as a complexing agent. However, the films obtained by CBD method are either amorphous or poorly crystallized. Therefore, annealing at high temperature was needed to improve the crystallinity of the thin films [11]. In addition, tri-sodium citrate can significantly improve the quality of the ZnS films obtained [12]. Göde et al. obtained hexagonal ZnS thin films using triethanolamine and tri-sodium citrate as complexing agents by CBD at 80 °C with 4.5 h [4]. For CIGS solar cells, the deposition time is too long for practical use in manufacturing.

In this paper we report some studies on chemical bath deposition of ZnS thin films from $\text{NH}_3/\text{SC}(\text{NH}_2)_2/\text{ZnSO}_4$ solutions. The CBD ZnS thin films characterization including structural, compositional and optical characterization are shown.

2. Chemical bath deposition of ZnS

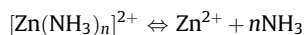
2.1. Reaction mechanism

Due to the fact that the solubility product, K_{sp} , for ZnS is low, $10^{-24.7}$ [13], ZnS precipitation can take place even at the lowest Zn^{2+} and S^{2-} ion concentration. Consequently, it is necessary to

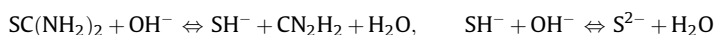
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control the free Zn^{2+} concentration by using suitable complexing agents, which release small concentrations of ions. In this study, NH_3 is used as complexing agent.

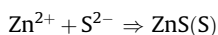
The process of CBD ZnS is similar to CBD CdS. First, the free Zn^{2+} is gained from the decomposition of various Zn-amine:



Thiourea has been used as the S^{2-} source through hydrolysis in alkaline medium:



The ZnS is formed by



When NH_3 as complexing agents, the Zn-amine is mostly in the form $[Zn(NH_3)_4]^{2+}$ with $10^{8.9}$ as the stability constant (k). CdS thin films are easily grown by CBD with NH_3 as the complexing agent. Thus, $[Cd(NH_3)_4]^{2+}$ is the major precursor in the heterogeneous growth of CdS thin films with $k = 10^{6.9}$. From these two values we can see that the deposition of ZnS by CBD is more difficult than that of CdS. In particular, it is evident that there is a much wider range of conditions in which the concurrent deposition of zinc sulfide or oxide can occur.

2.2. CBD growth of ZnS thin films

The depositions take place on commercial glasses. These were cleaned with detergent in an ultrasonic cleaner and finally dried with N_2 .

The solutions were prepared using analytical-grade reagents ($ZnSO_4$, thiourea, 25% ammonia). CBD ZnS thin films were chemically grown on glasses using a $ZnSO_4$ (0.010–0.100 M), ammonia (0.07–0.37 M), thiourea (0.8–4 M) aqueous solution at 80 °C.

The film thickness was measured using an AMBLOS XP-2 profilometer. X-ray diffraction patterns of the samples were recorded in Panalytical X'Pert Pro diffractometer with $Cu K\alpha$ radiation ($\lambda = 0.15418$ nm) source over the diffraction angle 2θ between 20° and 80°. The film composition was determined by X-ray fluorescence (XRF). The surface morphology of as-deposited ZnS films was studied using Hitachi S2400, scanning electron microscope (SEM). The transmission measurements were made by SBP300 spectrum instrument in the wavelength range from 300 to 1100 nm.

3. Results and discussion

3.1. Temperature influence

The growth on glass substrates as a function of deposition time has been studied for different temperature (Fig. 1). There we can see that the deposition process clearly shows three different growth phases, a none-film one, a quasi-linear one and a saturation one. In the none-film phase, there has no continuous film on the substrate. In the quasi-linear phase it is possible to calculate the initial growth rate. The behavior observed in the saturation region can be explained by taking into account the ZnS homogeneous precipitation which took place simultaneously to film deposition. The ZnS precipitation produces a fast consumption of the Zn^{2+} and S^{2-} free ions, and in a few minutes the ion precursors reach an equilibrium situation for a given deposition condition. From Fig. 1, we can expect a terminal film thickness normally between 120 and 140 nm.

In the quasi-linear region previous to the saturation region, film thickness can be controlled easily by deposition time control. In

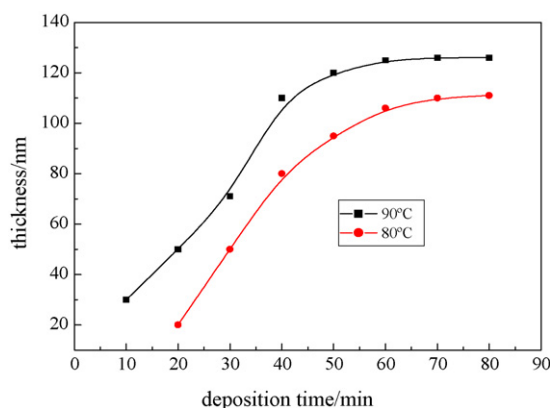


Fig. 1. Thickness variation with time of deposition at 80 and 90 °C ($[NH_3] = 2.9$ M, $[ZnSO_4] = 0.025$ M, $SC(NH_2)_2 = 0.2$ M).

this region, we can define the initial growth rate (r , expressed in nm/min).

We assume that the rate only depend on rate constant. According Arrhenius equation [14]:

$$r(t) = A \exp\left(\frac{-E_a}{RT}\right) \quad (1)$$

where $r(t)$ is the growth rate as temperature function for a given set of initial reagent concentration. A is a constant related with the initial reagent concentration, E_a is the activation energy, and R is the molar gas constant. Fig. 2 is represented the growth rate logarithm as a function of $1000/T$, for temperatures in the ranges 60–90 °C. The activation energy can be calculated from the slope of the linear fit of the logarithm of the initial growth rate as a function of $1000/T$. In this case, E_a showed a value around 7.65 kcal/mol. This low value of E_a shows that the rate-determining step in the deposition process is not a chemical one, in contrast with the results reported in the literature for CdS by CBD [15–17]. The determining step can be a physical step such as diffusion, adsorption, etc., for which lower activation energy values can be expected.

3.2. Influence of solution composition

The influence on the growth rate of the $ZnSO_4$ concentration at $[SC(NH_2)_2] = 0.27$ M, $[NH_3] = 2.9$ M, and the deposition temperature of 80 °C is represented in Fig. 3(a) and (b) represents the

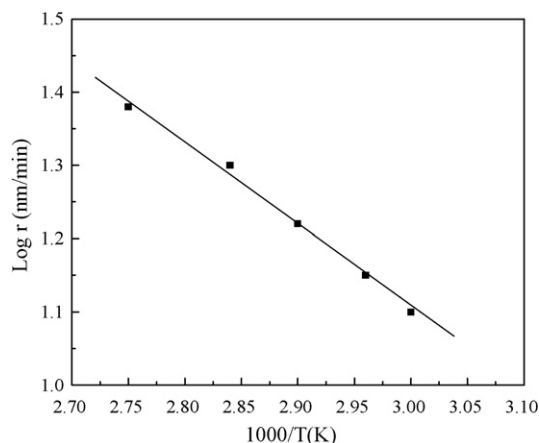


Fig. 2. Neperian logarithm of the initial growth rate against $1000/T$ (K) for samples prepared with at different temperatures.

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