

Research Article

Cd_{1-x}Zn_xS Thin Films with Low Zn Content Prepared by Chemical Bath Deposition

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Chemical bath deposition (CBD) was used for the growth of Cd_{1-x}Zn_xS thin films with low Zn content. The influence of preparation conditions, such as pH, temperature, and concentration, on film properties was investigated. The chemical growth mechanism of Cd_{1-x}Zn_xS thin films was analyzed, and optimized growth conditions for the thin films were established. The fill factor and short-circuit current were improved while Cd_{1-x}Zn_xS was used to replace CdS as the window layer in CdTe solar cells.

1. Introduction

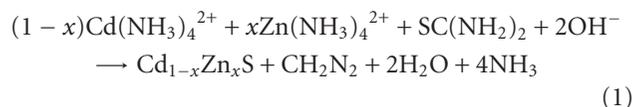
The highest conversion efficiency of CdS/CdTe thin film solar cells till now is 16.7% [1]. However, the band gap of CdS is not high enough so that the short wavelength photons are easy to be absorbed. The band gap of Cd_{1-x}Zn_xS varies in the range of 2.42 to 3.6 eV as zinc content increases [2]. While Cd_{1-x}Zn_xS is used to replace CdS as a window layer, not only the absorption of the window layer will be reduced, but also the short-circuit current of the Cd_{1-x}Zn_xS/CdTe thin film solar cells will be increased [3]. It is worth noting that two issues exist in the CdTe solar cells. One is the lattice parameter varying linearly with zinc content in the compound and thus resulting in a large lattice mismatch between Cd_{1-x}Zn_xS and CdTe. The other is the electrical resistivity increasing dramatically by the increase of zinc content [4]. Therefore, Cd_{1-x}Zn_xS at low Zn content is an ideal alternative material for CdTe thin film solar cells as the window layer.

Many ways, such as vacuum evaporation [4], chemical bath deposition [3, 5, 6] and, SILAR [7], have been used to prepare Cd_{1-x}Zn_xS thin films. Among these techniques, CBD presents many advantages: inexpensive, simple equipment, low temperature (<100°C), and large-area deposition. So it is well suited for the manufacture of photovoltaic devices [3, 5]. Because the solubility products of CdS ($K_{sp} = 10^{-28}$) and ZnS ($K_{sp} = 10^{-23.8}$) are different by several

orders of magnitude, the complexing agent is essential for codeposition of CdS and ZnS. In this work, NH₃ was used as the complexing agent to prepare Cd_{1-x}Zn_xS thin films at low Zn content. The influence of growth conditions on the properties of Cd_{1-x}Zn_xS was investigated to understand the deposition process and thus to improve the characteristics of the films. Subsequently Cd_{1-x}Zn_xS thin films were used as the window layer for the CdTe solar cells.

2. Experimental Details

In the CBD process, Cd_{1-x}Zn_xS thin films are prepared by slow release of S²⁻ and effective control of free Zn²⁺ and Cd²⁺ ions in the solution. The main chemical reactions happened in the solution can be described as follows:



In this work, a certain amount of ZnCl₂, CdCl₂, and NH₄Cl were dissolved in 200 mL DI water at room temperature. When the solution was heated to 60°C, a solution of ammonia was added to the solution and stirred for 5 min. Here the ammonia combines Cd²⁺ and Zn²⁺ to form the complex Cd(NH₃)₄²⁺ and Zn(NH₃)₄²⁺ which can constantly release Cd²⁺ and Zn²⁺. Then clean glass substrates or TCO-coated ones were placed vertically in the reaction

bath. Finally, a certain amount of thiourea was added to the solution, which slowly releases S^{2-} as a sulfur source. The rotating speed of the agitator during the deposition process was 30 r/min. The depositions were performed with $CdCl_2$, $ZnCl_2$, and $SC(NH_2)_2$ concentrations varying from 0.001 to 0.06 mol/L, ammonia concentrations in the range of 0.072 to 0.179 mol/L, and pH values between 8.5 and 10.5 to obtain the optimum growth conditions of the $Cd_{1-x}Zn_xS$ thin films. The values of pH were controlled by adding NH_4Cl to form a buffer solution with the desired pH. After a deposition of 1.5 hour, the substrates were released from the solution. One side was cleaned by HCl for testing convenience and then the substrates were deterged by DI water to remove the contaminant ions.

$CdTe$ solar cells with a $Cd_{1-x}Zn_xS$ layer (~ 180 nm) were fabricated for indicating the application of $Cd_{1-x}Zn_xS$ thin films. $CdTe$ films followed by the deposition of $Cd_{1-x}Zn_xS$ thin films were prepared by the close-spaced sublimation (CSS) technique. After CSS deposition of $CdTe$ with thickness of $8 \mu m$, the samples were treated in $CdCl_2$ vapor at $380^\circ C$ for 30 min. Then they were etched with Br-Methanol and rinsed in DI water and blown dry in N_2 . The back contact layer was formed by applying Sb_2Te_3 to the etched $CdTe$ surface and heat treating it in N_2 at $300^\circ C$ [8]. Finally, Au was used to complete the fabrication of $CdTe$ solar cells. For reference purpose, $CdTe$ solar cells with a CdS layer (~ 180 nm) were also fabricated.

The composition of the $Cd_{1-x}Zn_xS$ thin films was determined by X-ray fluorescence (XRF) measurements. The structural properties of the films were studied by X-ray diffraction (XRD). Measurement of the optical transmittance was made over the wavelength range 300~900 nm with a data interval of 1 nm. Scanning electron microscopy (SEM) was performed to investigate the surface morphology of the films. Electrical resistivity along the lateral direction was measured by depositing Al-stripes on the $Cd_{1-x}Zn_xS$ thin films and performing two-point probe measurements. The resulting PV devices were characterized using the light $J - V$ measurement under simulated AM 1.5 illumination (i.e., 100 mW/cm^2) with standard current-voltage measurement equipments.

3. Results and Discussions

3.1. Structural Properties. Figure 1 shows XRD patterns of $Cd_{1-x}Zn_xS$ thin films prepared at different pH values. It is found that the $Cd_{1-x}Zn_xS$ thin films are hexagonal with a preferential orientation along the (002) plane in the alkaline environment. When the pH value is 8.5, only a single strong $Cd_{1-x}Zn_xS$ (002) peak can be detected. However, as the pH value increases, the intensity of the $Cd_{1-x}Zn_xS$ (002) peak decreases and peaks of ZnS and ZnO also emerge in these patterns. This is probably caused by the excessive ammonia which leads to the reactions of $Zn(NH_3)_4^{2+}$ and OH^- , and that may be responsible for the accentuation of ZnO peak when the pH value increases to 9.5. When the pH value reaches up to 10.0, on the contrary, all the peaks are weakened.

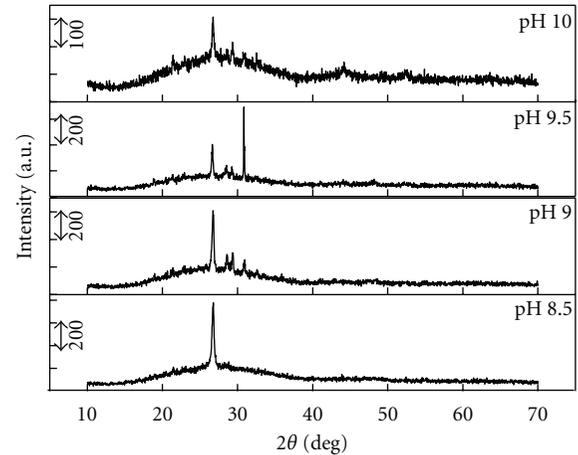


FIGURE 1: XRD patterns of $Cd_{1-x}Zn_xS$ thin films prepared at different pH values.

We investigate XRD patterns (not shown there) of $Cd_{1-x}Zn_xS$ thin films prepared at different temperatures. As the bath temperature increases from $60^\circ C$ to $90^\circ C$, the intensity of $Cd_{1-x}Zn_xS$ (002) firstly becomes strong and then weakens. Also, peaks other than $Cd_{1-x}Zn_xS$ cannot be detected in the thin films deposited at $70^\circ C$. Therefore, the optimal bath temperature to preparing $Cd_{1-x}Zn_xS$ thin films by CBD is $70^\circ C$.

As the buffering agent, NH_4Cl also affects the hydrolytic equilibrium of NH_4^+ ; therefore, it could balance the concentration of NH_3 to control the reaction rate. If no buffering agent is expected in the reactions, the deposition rate would be too fast at the beginning; however, it would be saturated quickly, and this is harmful to fabricate $Cd_{1-x}Zn_xS$ thin films with good quality. A suitable concentration of NH_4Cl enables the linear increase of deposition rate of $Cd_{1-x}Zn_xS$ thin films with the time, and that will be beneficial to deposit $Cd_{1-x}Zn_xS$ thin films [9]. When the concentration of NH_4Cl is 0.04 mol/L, the intensity of $Cd_{1-x}Zn_xS$ (002) peak is stronger than that of the concentrations of 0.03 and 0.05 mol/L. What is more, no obvious peak of $Cd_{1-x}Zn_xS$ (002) could be observed from the XRD patterns when the concentration of NH_4Cl changes to 0.025 mol/L or 0.055 mol/L. This is due to the insufficient buffering of NH_3 when the concentration of NH_4Cl is too low.

Usually, two mechanisms, homogeneous particles formation and heterogeneous surface reaction, are available when thiourea reacts with $CdCl_2$ and $ZnCl_2$. On the one hand, $[Cd(NH_3)_4]^{2+}$ and $[Zn(NH_3)_4]^{2+}$ combine with OH^- to form complexing ions. These ions are absorbed on the surface of the substrate, and then they react with thiourea to form metastable complex. Subsequently, the metastable complex decomposes to form a new $Cd_{1-x}Zn_xS$ surface. Therefore, the surface of $Cd_{1-x}Zn_xS$ thin films is compact and homogeneous (see Figure 2). On the other hand, the S^{2-} released from thiourea through hydrolysis reaction combines with free Cd^{2+} and Zn^{2+} ions to generate $Cd_{1-x}Zn_xS$ particles [10, 11]. These particles deposit on the surface of the substrate, which results in a rough and porous surface.

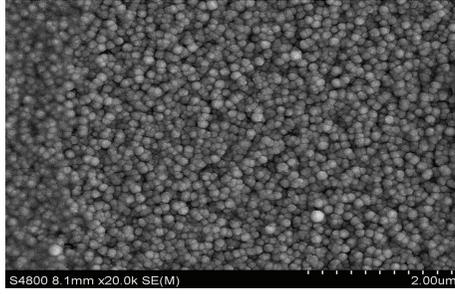


FIGURE 2: SEM Image of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films prepared by CBD.

By carefully controlling the bath concentration of thiourea, the reaction can be driven mainly as the heterogeneous mechanism. Hence, the structural properties of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films will be different. When the concentration of thiourea increases from 0.02 to 0.03 mol/L, the intensity of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ (002) peak is strengthened; however, as the concentration increases more, the peak height reduces lower and can hardly be differentiated from the background in XRD patterns.

Upon the previous analysis, it is found that the pH value, temperature, the bath concentration of NH_4Cl , or thiourea greatly affect the deposition of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films. As far as good crystallinity films are concerned, the standard conditions for growth of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films are $[\text{ZnCl}_2] = 0.001$ mol/L, $[\text{CdCl}_2] = 0.005$ mol/L, $[\text{NH}_4\text{Cl}] = 0.04$ mol/L, $[\text{SC}(\text{NH}_2)_2] = 0.03$ mol/L, $T = 70^\circ\text{C}$, and pH 8.5. In addition, we deposited $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films under these conditions and then annealed at 350°C in N_2 atmosphere. The XRD patterns of as-deposited and annealed $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films are shown in Figure 3. The diffraction peak positions do not change dramatically after annealing, but the average grain sizes of the films change from 17.5 to 32.8 nm according to Scherrer's equation.

3.2. Compositional Properties. The X-ray fluorescence analysis using the fundamental parameter (FP) method was used to determine the composition of the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films. Figure 4 gives the evolution of Zn content with the preparation conditions, that is, pH value, and the concentration of thiourea. It is found that, when the pH value increases, Zn content decreases, and the same situation is found when the temperature rises. Similarly, we varied the thiourea concentration, while the rest of the variables were maintained under the standard conditions. The Zinc content reaches up to 20 at% by increasing the thiourea concentration and then decreases. This is ascribed to the different solubility products of CdS and ZnS and the different stability constants for the cadmium and zinc precursors. For the standard conditions, $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films at $x \sim 20$ at% were obtained.

3.3. Electrical Properties. Figure 5 shows the plots of conductivity versus temperature for $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films. The conductivity of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films prepared at pH values varied from 8.5 to 9.5 increases monotonically as the temperature increases. The increase of σ with temperature

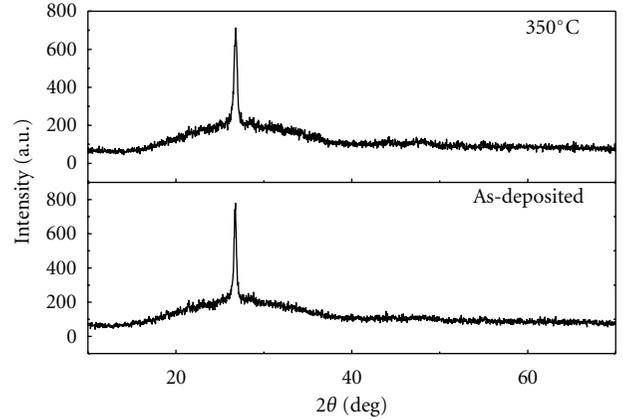


FIGURE 3: XRD patterns of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ prepared under the optimum conditions before and after annealing.

is ascribed to the growth of large grains, which increases the electron mean free path and reduces the scattering effect. However, for thin films prepared at pH 10, an abnormal behavior occurred in the range of $39\text{--}110^\circ\text{C}$. This phenomenon is also observed in CdS thin films [12, 13]. The relationship between σ and T can be described as

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right), \quad (2)$$

where σ_0 is constant, k is the Boltzmann constant, and E_a is activation energy. The values of E_a for thin films except for pH 10 are listed in Table 1. The thin films prepared at pH from 8.5 to 9.5 indicate three linear regions. The first at lower temperatures may be ascribed to the transitions from the impurity levels in the band gap to the bottom of the conduction band or the top of the valence band. The second is attributed to electron or hole transitions to the conduction or valence band. The third at higher temperatures is due to the electron transitions through the extended states in the conduction band [14].

3.4. Optical Properties. Considering the potential application of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin film as the window layer in CdTe thin film solar cells, it is necessary to investigate the influence of preparation conditions on the optical properties of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films. We varied one of the standard conditions while maintained other rest of variables. Figure 6 shows the transmittance of the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films prepared at different pH values. An extended spectral response for all the thin films at short wavelengths is noted. One can also see that the transmittance of the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films is higher than 60% when the wavelength is longer than 500 nm, in which the transmittance increases as the pH value decreases. For thin films prepared at pH 8.5 and 9.0, it is much higher than that of the other pH values. The same situation is found while varying the temperature, the concentration of NH_4Cl and thiourea. It seems that pH 8.5 or 9.0 is the optimum pH value. Using the Tauc equation, the band gap of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films is calculated by extrapolating the linear part of the curve to the $ah\nu$ axis, and the interception is the value of E_g .

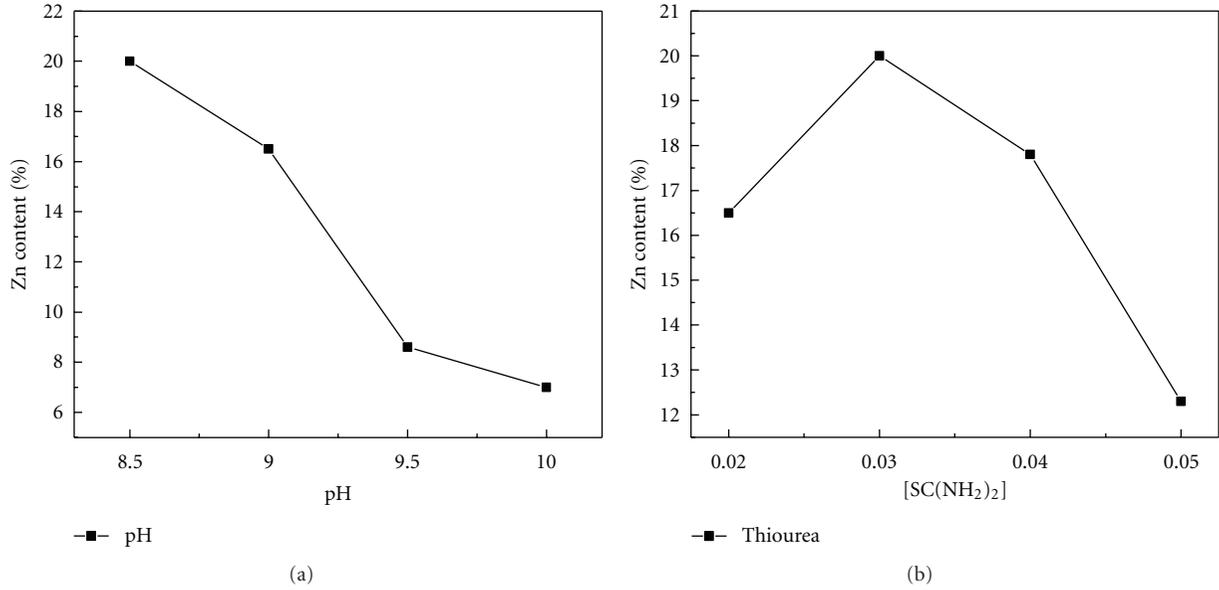


FIGURE 4: Plots of Zn content versus different deposition conditions of Cd_{1-x}Zn_xS thin films.

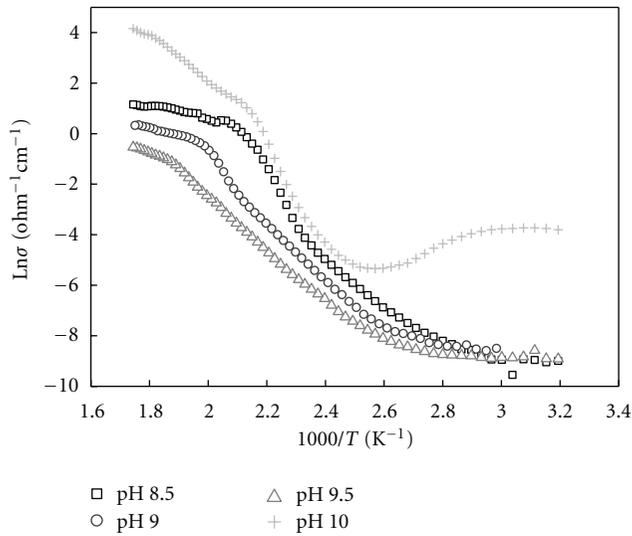


FIGURE 5: Variation of $\ln\sigma$ versus $1000/T$ for Cd_{1-x}Zn_xS prepared at different pH values.

From Figure 6, for thin films prepared at pH 9.5 and 10.0, they exhibit two absorption edges. The value of E_g can be calculated in the short wavelength regions to be about 3.6 eV. As evidenced by the XRD observations (see Section 3.1), we attribute it to the formation of ZnS or ZnO. The value of E_g for thin films prepared at pH 8.5 and 9.0 is about 2.56 eV, which is larger than that of CdS (~ 2.4 eV). That means Cd_{1-x}Zn_xS thin films prepared on these conditions may be better than CdS as the window layer of CdTe thin film solar cells.

From the properties of Cd_{1-x}Zn_xS thin films at low Zn content, we find that the standard conditions are the optimum ones for thin film deposition in fact.

TABLE 1: The values of activation energies for Cd_{1-x}Zn_xS prepared at different pH values.

pH	E_{a1} (eV)	E_{a2} (eV)	E_{a3} (eV)
8.5	0.57	1.67	0.24
9	0.22	1.01	0.29
9.5	0.13	0.86	0.43

3.5. Device Performance. CdTe thin film solar cells with the Cd_{1-x}Zn_xS window layer were fabricated based on the previous analysis. Table 2 shows the electrical parameters, for example, open circuit V_{oc} , short-circuit current density J_{sc} , fill factor FF , and conversion efficiency η for CdTe thin film solar cells with a Cd_{1-x}Zn_xS or CdS window layer. It is found that open circuit voltage changes very little, but the short circuit current for CdTe thin film solar cells with a Cd_{1-x}Zn_xS layer is higher than those with a CdS layer.

4. Conclusions

Cd_{1-x}Zn_xS thin films in the range of $x \leq 20$ at% were prepared by CBD. Under the optimum preparation conditions, the thin films were found to be hexagonal, which show highly preferential orientation. And the value of activation energies attributed to electron or hole transitions to the conduction or valence band is about 1.67 eV. The optical properties also show that the given preparation conditions are proper to deposit Cd_{1-x}Zn_xS thin films with high transmittance in both long and short wavelength ranges. Cd_{1-x}Zn_xS is used to replace CdS as the window layer; the fill factor and short-circuit current were improved, which means Cd_{1-x}Zn_xS thin films are more suitable for the window layer in CdTe solar cells.

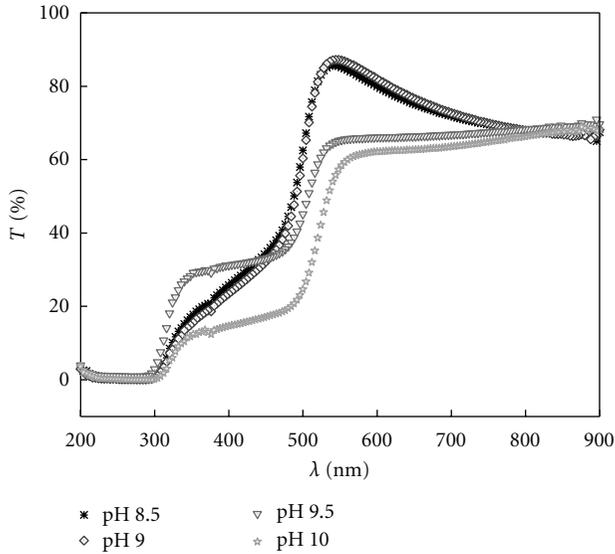


FIGURE 6: Transmittance curves of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films prepared at different pH values.

TABLE 2: Parameters for CdTe thin film solar cells.

Window layer	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF	η
$\text{Cd}_{1-x}\text{Zn}_x\text{S}$	691	22.1	58.5%	8.9%
CdS	681	19.7	53.2%	7.1%

Acknowledgments

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