Variations in the characteristics of Cd_xZn_{1-x}S films de-

WANG Yifan, XUE Yuming**, WANG Zhiyong, WEN Binbin, XIE Xin, and LÜ Chaoqun

posited with little Cd-containing solutions^{*}

Tianjin Key Laboratory of Film Electronic & Communication Devices, School of Integrated Circuit Science and Engineering, Tianjin University of Technology, Tianjin 300384, China

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In order to prepare $Cd_xZn_{1-x}S$ films with lower cadmium content and better performance as a buffer layer for copper indium gallium selenide (CIGS) solar cells, the performance of $Cd_xZn_{1-x}S$ films deposited in a mixture of solutions containing extremely low cadmium sources was systematically investigated by chemical bath deposition (CBD) with the synergy of chemical experiments and numerical simulations. The experimental results show that the films have the best overall performance at a cadmium source condition of 0.007 M.

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Cadmium sulfide (CdS) is an inorganic compound semiconductor belonging to group II-VI^[1]. High-purity CdS has a strong photoelectric effect on visible light, and is one of the common materials for preparing solar cells. However, CdS is a toxic carcinogen, which will pollute the environment and endanger human health^[2]. Second, the CdS's small band gap will inhibit the absorption of short wavelengths. As a result, zinc sulfide (ZnS), a different non-toxic and environmentally friendly semiconductor with a band gap of roughly 3.74 eV and strong short-wave transmittance^[3], is being explored as a possible replacement for CdS.

The ideal band gap of copper indium gallium selenide (CIGS), however, is around 1.35 eV, which differs significantly from the band gap of ZnS. This will cause lattice mismatch and lower the photoelectric conversion efficiency of thin film solar cells^[4]. According to research, doping zinc with CdS can modify the film's optical characteristics and band gap in order to lessen the impact of lattice mismatch and increase solar cell performance^[5]. Therefore, the ternary mixture $Cd_xZn_{1-x}S$, which shoulders multiple properties, has received much attention.

 $Cd_xZn_{1-x}S$ thin films can now be prepared using a variety of techniques, including radio frequency (RF) sputtering^[6], direct-current (DC) sputtering^[7], co-evaporation^[8], chemical bath deposition (CBD)^[9], and more. The CBD method's deposition process is straightforward and reasonably priced. Additionally, the CBD creates a film that causes the absorber layer relatively little harm, and its photovoltaic capabilities are easily altered by changing the experimental setup.

Currently, a high concentration of cadmium source solution is used in the majority of study literature on the effects of cadmium on the characteristics of Cd_xZn_{1-x}S films. For instance, the CBD method's most common cadmium source conditions range from 0.06 M to 0.9 M^[10], and the most common cadmium sources employed are cadmium nitrate solution, cadmium chloride solution, and cadmium sulfate (CdSO₄) solution. Additionally, although lower concentrations of cadmium source solution (0.003–0.007 M) were used in Ref.[11], the prepared films had poor characteristics, and the atomic percentage of cadmium in its solution gradually decreased with an increase in cadmium source content, which was quite different from the actual one. During the process of this research, the atomic percentage of cadmium grows with increasing concentration of the cadmium source, in contradiction to the experimental results of ZHANG et al^[11]. The impact of utilizing a relatively small quantity of cadmium (0.001-0.010 M) on the characteristics of Cd_xZn_{1-x}S films was assessed in this research. The characteristics of the created films were balanced, the ternary mixture's properties were maintained, and the amount of cadmium employed in the studies was successfully lowered, all of which have some bearing on the creation of buffer layers for CIGS solar cells.

The materials and concentrations required for the experiments are shown in Tab.1. CdSO₄, zinc sulfate (ZnSO₄), and ammonia sulfate ($(NH_4)_2SO_4$) were the major raw ingredients utilized in the experiment along with deionized water. Five clean beakers were configured with a mixed solution using the aforementioned

** E-mail: orwellx@tjut.edu.cn

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chemicals and the required amount of deionized water. The cleaned glass substrates were then put diagonally in the beakers, each measuring 3 cm×2 cm, and the beakers were then heated in a water bath. The required amounts of thiourea and ammonia were added to the beaker and carefully agitated after the solution's temperature reached 86 °C. The solution was agitated once every five minutes to achieve improved homogeneity during the 35 min deposition period.

Tab.1 Materials and concentrations required for the experiments

Material	Concentration (M)
CdSO ₄	0.001-0.010
$ZnSO_4$	0.015
$(NH_4)_2SO_4$	0.015
CH_4N_2S	0.03
NH ₃ ·H ₂ O	13.33

ZnSO₄, CdSO₄, and thiourea serve as sources of zinc ions, cadmium ions, and sulfur ions, respectively, in the process. $(NH_4)_2SO_4$ was employed as a buffer to control the emission rate of different metal ions and to make it easier to produce $Cd_xZn_{1-x}S$ films. Ammonia was also utilized as a complexing agent and pH regulator. The beakers were removed after 35 min of reaction time, and the samples were then cleaned with deionized water and dried with nitrogen.

These tools are available for thin film characterization. With scanning angles ranging from 3° to 120°, Rigaku's SmartLab 9 kW X-ray diffractometer (XRD) may be used to analyze the structural characteristics of thin films. The Quanta FEG 250 scanning electron microscope (SEM) from FIE and its associated energy dispersive spectroscopy (EDS) are used to examine the surface morphology and elemental composition of the films. Utilizing Perkin Elmer's Lambda ultra-violet, visible and near infrared (UV-Vis-NIR) spectrophotometry, the optical characteristics of the films were examined. Finally, the most recent SCAPS-1D-3.10 software was used to model the conversion efficiency of the thin film cells.

The surface morphology of the Cd_xZn_{1-x}S films developed under various settings with CdSO₄ concentration is depicted in SEM pictures in Fig.1. The general surface of both the film exhibits a dense and homogeneous morphology with extremely tiny holes between CdSO₄ concentrations of 0.005 M and 0.007 M, with 0.007 M providing the optimum surface morphology. However, around 0.003 M, the surface characteristics of the films began to alter as the concentration of CdSO₄ decreased, becoming loose and harsh with big holes. The small level of Cd²⁺ in the solution, which was unable to react with ammonia to create additional cadmium complexes, limited the formation of Cd_xZn_{1-x}S films at 0.001 M, resulting in the morphology of the films having a great deal of holes. And as the amount of CdSO₄ in the solution increased to 0.009 M and 0.010 M, the surface characteristics of the films also developed defects and pores. This was because there were too many cadmium ions in the solution, which led to the formation of a significant amount of chromium hydroxide precipitates in the solution and an increase in pH in the solution, both of which inhibited the growth of the films. These holes made it easier for carriers to combine, which decreased the efficiency of photoelectric conversion in thin film solar cells.



Fig.1 SEM images of the films deposited using different cadmium source conditions: (a) 0.001 M; (b) 0.003 M; (c) 0.005 M; (d) 0.007 M; (e) 0.009 M; (f) 0.010 M

The structural characteristics of the $Cd_xZn_{1-x}S$ films that were deposited under various cadmium source concentration conditions are shown by the XRD patterns in Fig.2. With the exception of the weak diffraction peaks of the films formed at 0.001 M concentration of the cadmium source, it can be shown that the films deposited at other concentrations exhibit a significant preferred orientation along the (002) plane of the hexagonal phase. The films' peak is around $2\theta=26.7^{\circ}$ for CdSO₄ concentrations ranging from 0.001 M to 0.007 M and 2θ =26.84° for concentrations between 0.009 M and 0.010 M. With respect to the provided XRD standard diffraction peak (002) of CdS with $2\theta=26.5^{\circ}$, the (002) peak location of $Cd_xZn_{1-x}S$ is displaced to a somewhat greater angle. When the cadmium source concentration is 0.001 M, the diffraction peak is weaker. This is brought on by the high concentration of zinc in the solution, which inhibits the formation of the cadmium complex and causes the deposition of $Cd_xZn_{1-x}S$ films to perform poorly. The (002) peak was strengthened and then diminished when the

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 $CdSO_4$ solution concentration was between 0.003 M and 0.010 M, and the greatest intensity of the diffraction peak was 0.007 M. It is clear from Tab.2's atomic percentage data and EDS results that the zinc concentration of the films had a bearing on their crystallinity. The film's crystallinity decreases with increasing zinc concentration.



Fig.2 XRD patterns of films deposited using different cadmium source conditions

Tab.2 Atomic ratios of Cd, Zn and S for films deposited using different cadmium source conditions

Different cadmium source conditions	S: Zn: Cd		
0.001 M	18.37: 46.86: 34.77		
0.003 M	19.22: 45.50: 35.28		
0.005 M	22.45: 39.42: 38.12		
0.007 M	29.74: 28.87: 41.39		
0.009 M	26.52: 33.10: 40.38		
0.010 M	26.55: 33.14: 40.31		

In Fig.3, the transmittance curves for the films created under various cadmium source conditions are displayed. As can be observed, all of the samples had high transmittance values of up to 90% at wavelengths longer than 450 nm. With a rise in the atomic percentage of cadmium in the solution, the transmittance of the materials at 0.001—0.010 M generally tends to decrease. In addition, the existence of larger holes on the surface of the films is the cause of the extremely high optical transmittance shown at 0.001 M and 0.010 M, but its practical value is lower.



Fig.3 Optical transmittance of the prepared films

Most of the valence band and conduction band electrons in semiconductors are located close to the forbidden band, allowing a large number of electrons to leap by absorbing photon energy when the photon energy is close to the forbidden band width. At this point, the absorption coefficient rises as the number of photons increases. The correlations between optical band gaps and absorption coefficients for semiconductor materials are as follows^[12],

$$(\alpha hv)^{\wedge}(\frac{1}{n}) = B(hv - E_g), \tag{1}$$

$$\alpha = -\frac{\ln(t)}{d},\tag{2}$$

where α , h and v represent the absorption coefficient, Planck's constant, and incident photon frequency, respectively ($v=c/\lambda$, where c is the speed of light, $c=3\times10^8$ m/s, and λ is the wavelength of incident light), B is the proportionality constant, and E_g is the forbidden band width of the semiconductor material. t is the film transmittance, and d is the film thickness. In addition, the value of n is related to the type of semiconductor material, n=1/2 when the semiconductor material is direct bandgap, and n=2 when the semiconductor material is indirect band gap^[13]. And n here is 1/2.

The $Cd_xZn_{1-x}S$ film's Tauc relationship curve is shown in Fig.4, using the values of $(a hv)^{1/n}$ as the vertical coordinate and *h* as the horizontal coordinate. Then, a linear equation can be found as follows

$$y = C(x - E_g), \tag{3}$$

where $E_{\rm g}$ in a geometric sense refers to the line's intercept on the x-axis. In other words, the linear portion of the line is linearly fitted to obtain a linear equation that intersects the x-axis, and the x-value of the intersection point is the desired optical band gap size. According to the images, the optical band gaps are 3.72 eV, 3.62 eV, 3.46 eV, 3.02 eV, 3.22 eV, and 3.32 eV, respectively, for cadmium source concentrations of 0.001 M, 0.003 M, 0.005 M, 0.007 M, 0.009 M, and 0.010 M. With the help of the data from the EDS, it is possible to see that the optical band gap decreases and then increases as the concentration of cadmium ions rises. The band gap trend is consistent with the trend of the atomic percentage content of zinc in the solution, indicating that changes in zinc content can affect the band gap of the film and alter its transmittance.

For thin film solar cells, the solar cell simulation program (SCAPS-1D) is ideal for evaluating the *J-V* curve, *QE* curve, V_{oc} , J_{sc} , *FF*, and many other measurements of solar cells, which can also mimic the performance of the manufactured films. Mo/CIGS/CdS/ZnO is the CIGS structure that is utilized in Ref. [12], and Tab.3 displays the fundamental characteristics of each layer that may be found in many literatures, where neutral is selected as the defect type, 0.6 is the reference energy level, and 0.1 is the characteristic energy. Other default settings and the • 0362 •

AM1 5G spectrum are also utilized for the simulation test^[14]. Tab.4 displays the findings of the final experiment, V_{oc} is stable at 0.8 V, J_{sc} is around 38 mA/cm², and *FF* is up to 81%, as can be observed. Additionally, when the cadmium source concentration is 0.001 M, the efficiency can increase to up to 24.34%. However, the conversion efficiency is excellent at the cadmium source concentration of 0.007 M, which may reach 24.20%, when taking the combined SEM and XRD data into account. The experimental findings indicate that the films created under low cadmium source conditions have excellent potential for use as the buffer layer in CIGS solar cells.

In this study, the synergistic impact of chemical tests and numerical simulations was used to evaluate the effect





Fig.4 Tauc plot of films deposited using different cadmium source conditions: (a) 0.001 M; (b) 0.003 M; (c) 0.005 M; (d) 0.007 M; (e) 0.009 M; (f) 0.010 M

Parameter	CIGS ^[15]	ZnO ^[16]	CdZnS ^[17]
Thickness (nm)	1 550	80	Variable
$E_{\rm g}({\rm eV})$	1.2	3.3	Variable
χ (eV)	4.6	4.4	4.2
\mathcal{E}_{r}	9	9	9.2
$N_{\rm c}~({\rm cm}^{-3})$	2.2×10^{18}	2.0×10 ¹⁸	2.1×10^{18}
$N_{\rm v}({\rm cm}^{-3})$	1.5×10 ¹⁹	2.0×10 ¹⁹	1.7×10^{19}
$\mu_{\rm e} ({\rm cm}^2/{\rm Vs})$	100	100	70
$\mu_{\rm h}({\rm cm}^2/{\rm Vs})$	11.5	20	20
$N_{\rm D}~({\rm cm}^{-3})$	-	5.0×10 ¹⁷	1×10^{16}
$N_{\rm A}~({\rm cm}^{-3})$	2.0×10^{17}	-	-

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Tab.4 Simulation data obtained by the software

$C(Cd^{2+})(M)$	$V_{\rm OC}({ m V})$	$J_{\rm SC}$ (mA/cm ²)	FF (%)	ETA (%)
0.001	0.800 3	38.880 12	81.46	24.34
0.003	0.800 3	38.851 10	81.42	24.31
0.005	0.800 6	38.825 22	81.42	24.20
0.007	0.800 8	38.821 16	81.41	24.20
0.009	0.800 9	38.810 28	81.41	24.17
0.010	0.800 9	38.810 26	81.41	24.16

of decreased cadmium content in the mixed solution on the film performance, with a focus on both environmental protection and film performance. The experimental findings demonstrate the superior performance of the produced $Cd_xZn_{1-x}S$ films, with conversion efficiencies up to 24.20% at 0.007 M cadmium source conditions. The films exhibit a superior optical band gap of 3.02 eV, improved surface shape and crystallinity, and high transmittance at this concentration.

Ethics declarations

Conflicts of interest

The authors declare no conflict of interest.

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