Conflict of Interest:

The authors declare that they have no conflict of interest.

Effect of concentration of cadmium sulfate solution on structural,optical and electric properties of $Cd_{1-x}Zn_xS$ thin films

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ABSTRACT

$Cd_{1-x}Zn_xS$ thin films were deposited by chemical bath deposition (CBD) on glass substrate to study the influence of cadmium sulfate concentration on the structural characteristics of the thin film. The SEM results show that the thin film surfaces under the cadmium sulfate concentration of 0.005 M exhibit better compactness and uniformity. Due to the less Cd^{2+} involved in the reaction and little precipitation in the solution. The distribution diagrams of thin film elements illustrate that the film growth rate changes on the increase, decrease, and increase with the increase of cadmium sulfate concentration. XRD studies exhibit the crystal structure of the film is hexagonal phase, and there are obvious diffraction peaks and better crystallinity when the concentration is 0.005 M. Spectrophotometer test results demonstrate that the relationship between zinc content x and optical band gap value E_g can be expressed by the equation $E_g(x)=0.59x^2+0.69x+2.43$. Increasing the zinc content can increase the optical band gap, the absorbance of the thin film can be improved by decreasing the cadmium sulfate concentration, however, all of them have good transmittance. At a concentration of 0.005 M, the thin film has good absorbance in the 300 - 800 nm range, 80% transmittance, and band gap value of 3.24 eV, which is suitable for use as a buffer layer for solar cells.

Keywords:CIGS thin film solar cell; CBD(Chemical bath deposition); Buffer layer; $Cd_{1-x}Zn_xS$ thin films; Cadmium sulfate

1. Introduction

CdS, an N-type direct band-gap semiconductor material with an optical band gap of 2.43 eV and a good transmittance in the visible light range, has been studied as a buffer layer for heterojunction solar cells for many years [1]. However, due to the narrow optical band gap of CdS, the absorption layer of short wave is hindered. In addition, cadmium is a toxic substance that is detrimental to human health. An environmental friendly N-type semiconductor compound ZnS, with an optical band gap of 3.71 eV [2] and a good transmittance for short wave, has been widely considered to replace CdS. While, copper indium gallium selenide (CIGS) band gap values range from 1.02 eV to 1.67 eV, there is a big difference between them. Direct contact results in poor lattice matching with the solar cell absorption layer [3], affecting

modules photoelectric conversion efficiency. Studies have found that the band gap of CdS can be adjusted by doping Zn to improve the thin film performance [4], and sulfur heterojunction materials containing cadmium and zinc can be prepared in the form of $Cd_{1-x}Zn_xS$. Due to the doping of Zn, the band gap of the thin film varies between 2.43 eV and 3.71 eV. The photoelectric properties of the thin film can be improved by regulating the proportion of zinc in the thin film properly.

A number of methods have been developed for preparing $Cd_{1-x}Zn_xS$ thin films including spray pyrolysis, Successive Ion Layer Absorption and Reaction (SILAR), chemical vapor deposition (CVD) and chemical bath deposition (CBD) [5], etc. The CBD method is adopted in experimental research for its low-cost and relatively reduced damage to absorption layer. The quality of the thin film prepared by this method is affected by the following factors, for example, concentration of reaction solution, temperature, pH value and the Cd^{2+} concentration [6]. Olivia et al. concluded that the surface morphology of CdZnS films with low cadmium ion concentration was better than that of films with high cadmium ion concentration [7]. Zhang used CBD to deposite $Cd_{0.9}Zn_{0.1}S$ thin film with the band gap of 2.56 eV, exhibiting high transmittance and dense surface. Solomon U. Offiah et al. thought that higher Cd source concentrations were favorable for single-phase deposition of CdZnS films, and the optical band gap increased with the increase of cadmium source concentration [8].

Although studies on the effects of cadmium ion concentration on $Cd_{1-x}Zn_xS$ thin films have been extensively reported, the sources of cadmium are mostly cadmium chloride ($CdCl_2$), cadmium nitrate ($Cd(NO_3)_2$) or cadmium acetate ($Cd(CH_3CO_2)_2$), and little research has been conducted on the effects of cadmium sulfate ($CdSO_4$) on thin films. In this paper, the influence of cadmium sulfate concentration on the morphology structure and optical properties of $Cd_{1-x}Zn_xS$ thin films is studied, aiming to improve the properties of thin films.

2. Experimental

2.1 $Cd_{1-x}Zn_xS$ films deposited by chemical bath deposition (CBD)

Part of the ions of insoluble substances enter the solution and the others deposit on the solid surface. The dissolution equilibrium is reached when rate is the same in both, and the equilibrium constant is called solubility product [9]. However, materials prepared by CBD process generally have a small solubility product, once Cd^{2+}, Zn^{2+} and S^{2-} is presented in the solution, precipitation will be generated rapidly, affecting the growth of thin films. Thus, complexing agents are usually added to reduce metal ion release rate. Ammonia is generally chosen as complexing agent and ammonium sulfate as buffer. NH_4^+ reacts with Cd^{2+} and Zn^{2+} to form a stable complex of cadmium and zinc for controlling the film deposition rate effectively and improving the film growth quality.

Table 1

Deposition conditions of CBD-$Cd_{1-x}Zn_xS$.

Reagents	Concentration
$ZnSO_4$	0.020M
$(NH_4)_2SO_4$	0.025M
$SC(NH_2)_2$	0.015M
$NH_3.H_2O$	25%
$CdSO_4$	0.003M、0.004M、0.005M、0.006M、0.007 M

The reagents used under experimental growth conditions of $Cd_{1-x}Zn_xS$ thin films are shown in Table 1. In this experiment, cadmium sulfate and zinc sulfate are used as the source of Cd^{2+} and Zn^{2+}, thiourea as the source of S^{2-}. Besides, ammonia water is used as the complexing agent and ammonium sulfate as the buffer agent. During the experiment, the 2 cm×3 cm glass substrates that cleaned with deionized water ultrasonic cleaning solution are put into five beakers, followed by the addition of cadmium sulfate, zinc sulfate, ammonium sulfate and appropriate amount of deionized water. Adding 25% ammonia and 1M thiourea in turn when the temperature of the reaction liquid water reaches to 85°C, and timing is started. The mixture is stirred every 5 minutes, and yellow precipitation gradually formed in the beakers. After 30 minutes of reaction, take out the beakers, wash and dry the samples. The chemical reactions during the deposition of the film are as follows:

$$NH_3+H_2O\rightarrow NH_4^++OH^- \quad (1)$$

$$ZnSO_4\rightarrow Zn^{2+}+SO^{2-} \quad (2)$$

$$Zn^{2+}+4NH_3\rightarrow [Zn(NH_3)_4]^{2+} \quad (3)$$

$$CdSO_4\rightarrow Cd^{2+}+SO^{2-} \quad (4)$$

$$Cd^{2+}+4NH_3\rightarrow [Cd(NH_3)_4]^{2+} \quad (5)$$

$$(NH_2)_2CS+2OH^-\rightarrow S^{2-}+2H_2O+CH_2N_2 \quad (6)$$

$$[Cd(NH_3)_4]^{2+}+[Zn(NH_3)_4]^{2+}+S^{2-}\rightarrow Cd_{1-x}Zn_xS+\text{waste} \quad (7)$$

2.2 Characterization of $Cd_{1-x}Zn_xS$ thin films

The surface morphology of the film is studied by scanning electron microscope (SEM 460L03040702), Energy Dispersion Spectroscopy (EDS) attached to the Environment Scanning Electron Microscope with a field emission gun (Quanta-FEG 250) is used to analyse the composition and element content of the thin film. A study is made on the crystal structure of the thin film by using X-ray diffraction (XRD) with a scanning range of 10 deg to 70 deg, a step length of 0.02, a voltage of 40 kV and a current of 200 mA. The thin film thickness data are recorded with step height measuring instrument (Veeco Dektak 150). The optical properties of the thin film are

studied by UV-Vis-NIR spectrophotometer at the wavelength range of 300 - 800 nm.

3. Results and discussion

3.1 Film thickness

Table 2 reveals the thickness of the film obtained by the step height measurement instrument. With the increase of cadmium sulfate concentration, the thickness of the film first increase, then decrease and increase again, indicating that the film growth rate changes on the increase, decrease, and increase. Due to the augment of zinc content hinders the reaction between Cd^{2+} and NH_3 to form the cadmium complex, the release rate of cadmium and zinc ions in the solution is accelerated, resulting in the formation of precipitation rate faster than that of the formation of $Cd_{1-x}Zn_xS$ thin films, the thin film growth rate decreases, the film becomes thinner.

Table 2

Thickness of $Cd_{1-x}Zn_xS$ thin films with different cadmium sulfate concentration.

Concentration of cadmium sulfate (M)	Thickness (nm)
0.003	71.13
0.004	73.28
0.005	64.73
0.006	62.46
0.007	66.51

3.2 Surface morphology

Fig. 1(a), (b), (c), (d), (e) exhibits the surface morphology of $Cd_{1-x}Zn_xS$ thin films deposited under the concentration of 0.003 M, 0.004 M, 0.005 M, 0.006 M, 0.007 M cadmium sulfate respectively. It can be seen that the $Cd_{1-x}Zn_xS$ thin films with cadmium sulfate concentration of 0.003 M, 0.004 M, and 0.007 M present better uniformity. For the reason that there's less Cd^{2+} in the solution. Due to the addition of complexing agent, the release rate of metal ions slows down, Cd^{2+} react with OH^- to produce less precipitation of $Cd(OH)_2$, while the complex ions react with S^{2-} to form $Cd_{1-x}Zn_xS$. The accelerated growth rate making the film with fewer pores and better density. With the increase of cadmium sulfate concentration, excessive Cd^{2+} exists in the solution. The precipitation of $Cd(OH)_2$ and $Zn(OH)_2$ increases rapidly, hindering the film's growth, the solution alkalinity increases, leading to more pores. When the concentration continues to increase to 0.007 M, less Cd^{2+} and S^{2-} involved in the reaction results in accelerated the film growth rate and improved compactness. Since pores increase the probability of carrier recombination and reduce the photoelectric conversion efficiency, thin films with fewer pores on the surface are more suitable for the buffer layer.

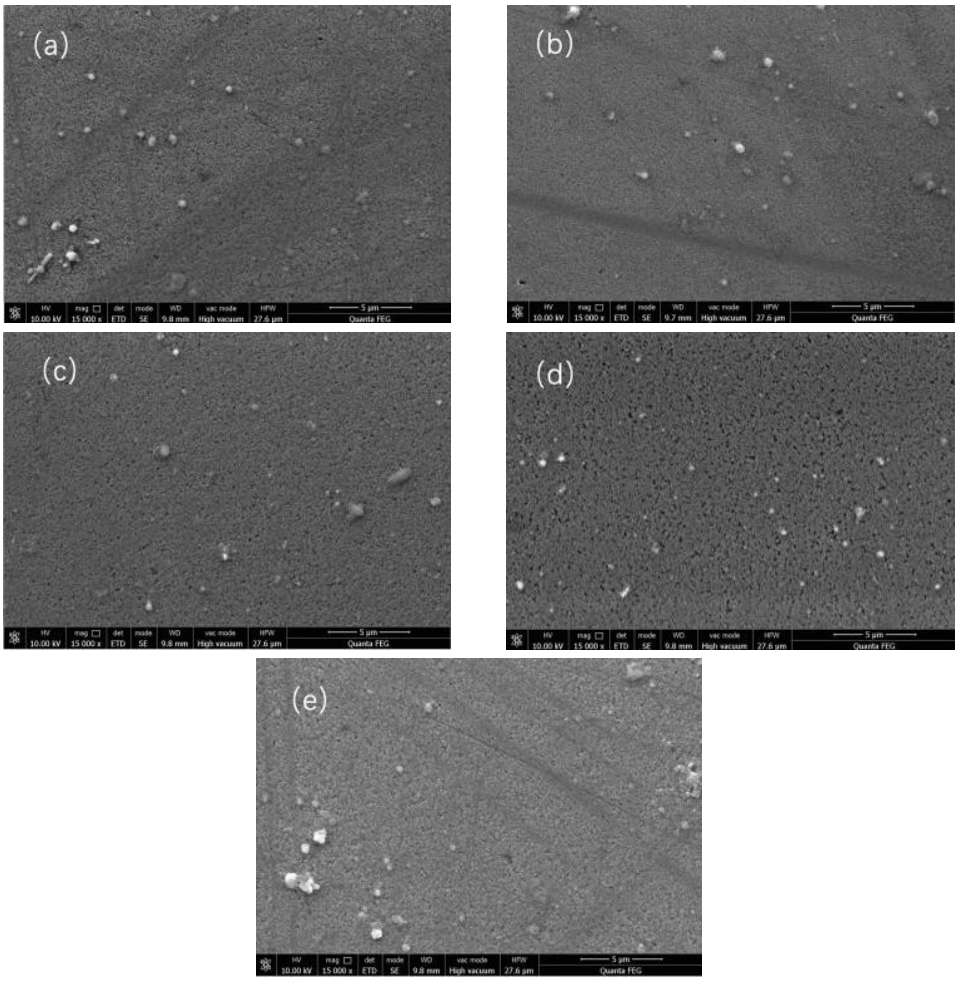
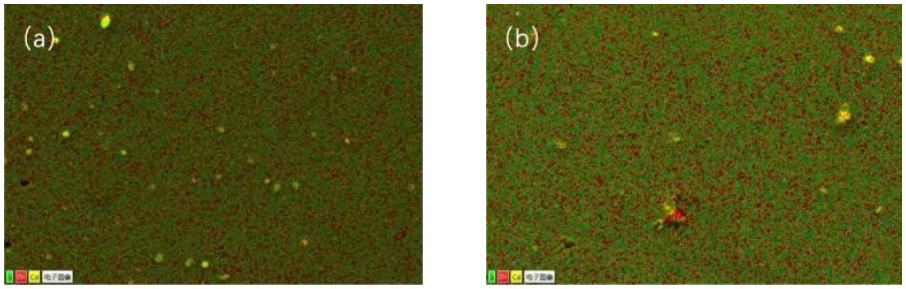


Fig. 1. SEM images of $Cd_{1-x}Zn_xS$ thin films prepared with different concentrations of cadmium sulfate.

3.3 Thin film composition

The distribution diagrams of Cd, S and Zn in $Cd_{1-x}Zn_xS$ films deposited under the different concentration of cadmium sulfate are showed in Fig. 2, in which yellow represents cadmium, red represents zinc, and green represents sulfur. The (c) and (d) diagrams show strong red, corresponding to $CdSO_4$ concentration of 0.005 M and 0.006 M, while graphs (a), (b) and (e) show more green and yellow, corresponding to $CdSO_4$ concentration of 0.003 M, 0.004 M and 0.007 M. The above phenomenon indicates that zinc content changes on decrease, increase and decrease, it is preliminarily concluded that it is formed due to the augment of the cadmium sulfate concentration.



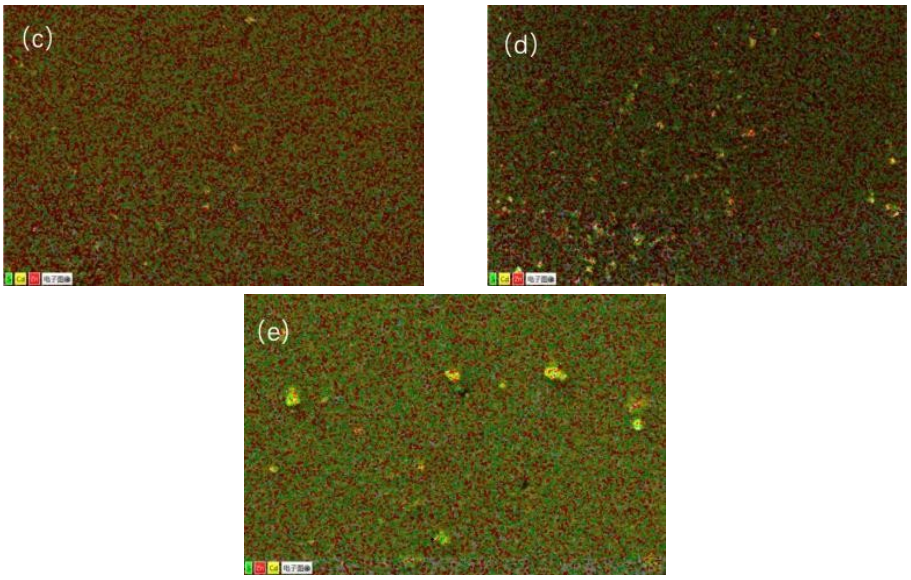


Fig. 2. Element distribution diagrams of $Cd_{1-x}Zn_xS$ thin films deposited with different concentrations of cadmium sulfate.

Table 3

The atom ratios of S, Zn and Cd in $Cd_{1-x}Zn_xS$ thin films prapared with different concentrations of cadmium sulfate.

Concentration of cadmium sulfate (M)	Atom ratios of S, Zn and Cd	Zn/(Zn+Cd)
0.003	30.40 : 36.81 : 32.79	0.529
0.004	31.87 : 34.34 : 33.79	0.504
0.005	22.17 : 55.83 : 22.00	0.717
0.006	22.61 : 57.24 : 20.15	0.739
0.007	28.82 : 37.92 : 33.26	0.533

The EDS data given in Table 3 show that with the increase of $CdSO_4$ concentration, the percentage of zinc content presents a trend of decrease, increase and decrease.

When the concentration of $CdSO_4$ increases to 0.004 M, the complex of cadmium in the solution increases and reacts with S^{2-} to form $Cd_{1-x}Zn_xS$. The addition of complexing agent reduces the release rate of metal ions, results in less precipitation and slightly increased the film growth rate. EDS results show the percentage of zinc decreases slightly, indicating that it is related to the film growth rate. When the concentration increases to 0.005 M, cadmium and zinc ions react with OH^- to form the precipitation of $Cd(OH)_2$ and $Zn(OH)_2$ rapidly, making the film growth rate slows down and the percentage of zinc content increases significantly. The same is true when concentration adds to 0.006 M. While it continues to increase to 0.007 M, due to the excessive consumption of Cd^{2+} and S^{2-} involved in the reaction and little precipitation in the solution, the film growth rate accelerates, and the percentage of zinc content decreases rapidly. It is confirmed that the increasing cadmium sulfate

concentration results in the changing trend of zinc content in the film, so does the film growth rate. The growth of thin films is inhibited with the increase of zinc content.

3.4 Crystal structure characteristics

XRD pattern of $Cd_{1-x}Zn_xS$ films prepared under the different $CdSO_4$ concentrations are shown in Fig. 3. It can be seen visually that diffraction peaks appear at position 2θ=27.020 corresponding to concentration of 0.004 M and 0.005 M. This demonstrates that the film crystallinity under this concentration is better than other concentrations. There is a strong preferential orientation on the (002) plane of the hexagonal phase. It can be seen that the (002) peak position of $Cd_{1-x}Zn_xS$ generated at the five cadmium sulfate concentration is shifted to a higher angle with respect to 2θ=26.507 corresponding to the XRD standard diffraction peak (002) of the given CdS. Due to the addition of ZnS, while the lattice constant of hexagonal phase ZnS is smaller than that of hexagonal phase CdS , thus the lattic constant of the $Cd_{1-x}Zn_xS$ thin film is smaller than CdS, making the (002) peak shifts to a higher angle. It can be concluded from EDS results that the thin film crystallinity is related to the zinc content. The higher the zinc content is, the worse thin film crystallinity will be. For the reason that the increasement of zinc content hinders the reaction between Cd^{2+} and NH_3 to form a cadmium complex and accelerates the release rate of metal ions, leading to more precipitation in the solution, the worse density of the thin film and the lower diffraction peak [10].

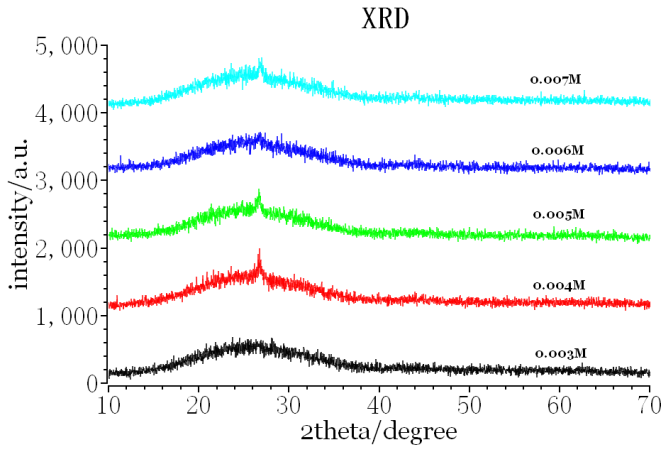


Fig. 3. XRD patterns of $Cd_{1-x}Zn_xS$ thin films deposited at different concentrations of cadmium sulfate.

3.5 Optical properties

The optical properties of the thin film are studied by using ultraviolet visible near infrared spectrophotometer. The absorbance is shown in Fig. 4(a). In the figure, the thin film has a higher absorbance at the wavelength of less than 500 nm than that of more than 500 nm, and the absorbance decreases sharply in the wavelength range of 300 - 350 nm. The absorbance gradually increases as the cadmium sulfate concentration increases, while it decreases at the concentration of 0.007 M.

The light transmittance is exhibited in Fig. 4(b). The transmittance of the thin film increases sharply with the increase of the wavelength in the range of 300 - 500 nm, and rises slowly when exceeding 500 nm. The thin films prepared under the five cadmium sulfate concentrations have good transmittance, the everage transmittance within visible light range is over 80%. Especially when concentration is 0.007 M, it exceeds 85%. In addition, the absorbance edge of the film presents significant blue shift as the change of cadmium sulfate concentration [11].

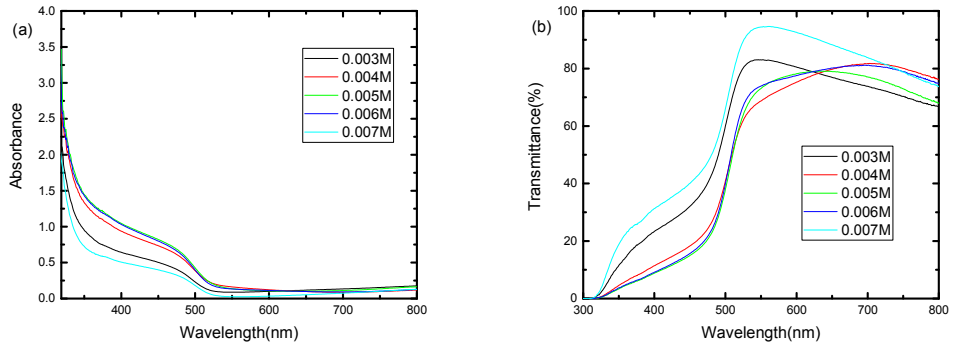
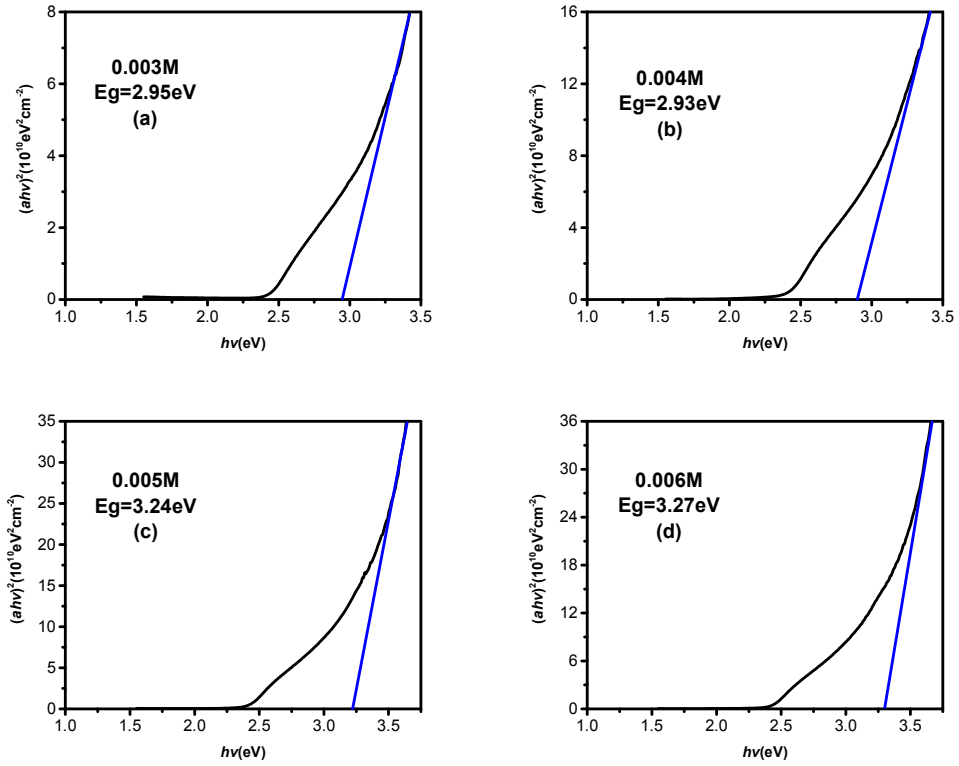


Fig. 4. Plot of (a) absorbance vs wavelength (b) transmittance vs wavelength for the $Cd_{1-x}Zn_xS$ thin films prepared with different concentrations of cadmium sulfate.

3.6 Electrical properties



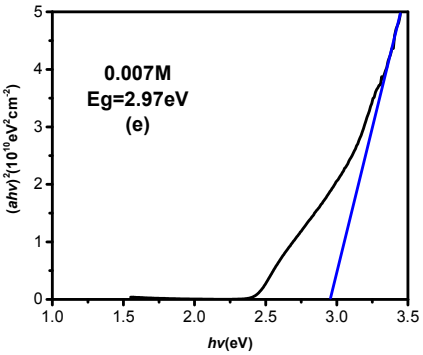


Fig. 5. Band gap of Cd1-xZnxS thin films deposited with different concentrations of cadmium sulfate.

The optical band gap and absorption coefficient of the $Cd_{1-x}Zn_xS$ thin films satisfy the Tauc equation [12]:

$$(\alpha hv)^{1/n} = A(hv - Eg) \tag{8}$$

Where α is the absorption coefficient, *hv* is photon energy, E_g is the optical band gap and A is a constant. Depending on the type of semiconductor, the exponential n is 1/2 for the direct band-gap semiconductor and 2 for the indirect band-gap semiconductor [13]. Since $Cd_{1-x}Zn_xS$ is a direct band-gap semiconductor, the value of n is 1/2.

While the absorption coefficient α can be calculated by formula (9):

$$\alpha = -\ln(T)/d \tag{9}$$

Where T is the light transmitance, d is the thin film thickness. α is calculated by formula (9), then bring it into formula (8) and draw the $(\alpha hv)^2$-hv scatter diagram, which is shown in Fig. 5. In the figure, the straight line is the tangent line of the curve, the extension line intersects with the horizontal axis, and the abscissa of the intersection is the thin film optical band gap. According to this, the thin film band gaps corresponding to the $CdSO_4$ concentration of 0.003 M, 0.004 M, 0.005 M, 0.006 M and 0.007 M are 2.95 eV, 2.93 eV, 3.24 eV, 3.27 eV and 2.97 eV. It can be observed that with the increase of cadmium sulfate concentration, the band gap changes on decrease, increase and decrease. The change trend of it is consistent with that the percentage of zinc atoms, indicating that the zinc content is closely related to the band gap.

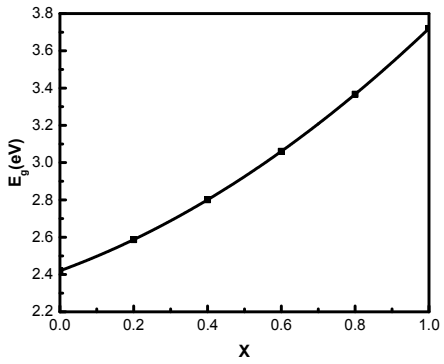


Fig. 6. The value of $Cd_{1-x}Zn_xS$ thin film band gap changes with x

Table 4

Film element content, zinc-cadmium content ratio and band gap.

Cd(at.%)	Zn(at.%)	S(at.%)	Zn/Cd	$Cd_{1-x}Zn_xS$	E_g(eV)
32.79	36.81	30.40	1.12	$Cd_{0.48}Zn_{0.52}S$	2.95
33.79	34.34	31.87	1.02	$Cd_{0.50}Zn_{0.50}S$	2.93
22.00	55.83	22.17	2.54	$Cd_{0.28}Zn_{0.72}S$	3.24
20.15	57.24	22.61	2.84	$Cd_{0.26}Zn_{0.74}S$	3.27
33.26	37.92	28.82	1.14	$Cd_{0.47}Zn_{0.53}S$	2.97

It can be intuitively seen from Fig. 6 that the thin film band gap values varies between 2.43 eV and 3.71 eV at different cadmium sulfate concentrations. When x=0, the film is undoped with zinc, the band gap value is 2.43 eV; while x=1, the band gap value is 3.71 eV. Fig. 6 shows the thin film band gap values changes with x, which is nonlinear. Further studies have found that there is a certain functional relationship between the two, which can be expressed by the dielectric model and the pseudopotential model [14]. They satisfy the following equation:

$$E_g(x) = kx^2 + (E_{g,ZnS} - E_{g,CdS} - k)x + E_{g,CdS} \quad (10)$$

Where $E_{g,CdS}$ and $E_{g,ZnS}$ represent the band gap values of CdS and ZnS in $Cd_{1-x}Zn_xS$, K represents the bending coefficient, which can be calculated by the following formula [15]:

$$k = 4[0.5(E_{g,CdS} + E_{g,ZnS}) - E_{g,0.5}] \quad (11)$$

$E_{g,0.5}$ represents the band gap value when x=0.5. Through the analysis of the atomic percentage and the film band gap, results are exhibited in Table 4. Eventually, the nonlinear relationship between $Cd_{1-x}Zn_xS$ thin film band gap value E_g and x can be expressed as:

$$E_g(x)=0.59x^2+0.69x+2.43 \quad (12)$$

According to equation (12), increasing the zinc content in the thin film will increase the optical band gap. Due to the addition of Zn, the band gap of the thin film varies between 2.43 eV and 3.71 eV. The proportion of zinc element in the thin film can be adjusted properly to match the energy band between the buffer layer and the

absorption layer, increase the thin film absorbance and improve the photoelectric properties.

4. Conclusion

The zinc content affects the compactness and the growth rate of the thin film. The lower the zinc content is, the denser the thin film and the faster the growth rate will be. It can be seen from the SEM results that the surface of the thin film prepared under the cadmium sulfate concentration of 0.005 M is relatively dense. For the reason that less Cd^{2+} is involved in the reaction and little precipitation in the solution. The changes of cadmium sulfate concentration affect the thin film growth rate. In the process of increasing the concentration, the growth rate changes on increase, decrease and increase, due to the precipitation in the solution changes from less to more and less. XRD results indicate that the zinc content affects crystallinity, the higher the zinc content is, the worse the crystallinity will be. According to UV-Vis-NIR spectrophotometer data, the proportion of zinc x is related to the optical band gap value E_g, which satisfy the equation $E_g(x)=0.59x^2+0.69x+2.43$. Increasing the zinc content will improve the optical band gap, absorbance and transmittance. When the cadmium sulfate concentration is 0.005 M, the thin film has good absorbance, 80% transmittance, and band gap value of 3.24 eV, which is suitable for use as a buffer layer for solar cells.

Acknowledgements

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References

[1]Abza T, Ampong F K, Hone F G, et al. Preparation of cadmium zinc sulfide (Cd1−xZnxS) thin films from acidic chemical baths[J]. Thin Solid Films, 2018, 666: 28-33.

[2]Zellagui R , Dehdouh H , Adnane M , et al. CdxZn1-xS thin films deposited by Chemical Bath Deposition (CBD) method[J]. Optik - International Journal for Light and Electron Optics, 2020, 207:164377.

[3]Ma L, Ai X, Wu X. Effect of substrate and Zn doping on the structural, optical and electrical properties of CdS thin films prepared by CBD method[J]. Journal of Alloys and Compounds, 2017, 691: 399-406.

[4]Bae D , Gho J , Shin M , et al. Effect of zinc addition on properties of cadmium sulfide layer and performance of Cu(In,Ga)Se2 solar cell[J]. Thin Solid Films, 2013, 535(may 15):162-165.

[5]Chen, Y, X,etal. Preparation and characterisation of CdxZn1-xS thin films grown in chemical bath deposition[J]. Materials Research Innovations, 2015.

[6]Guo W , Xue Y M , Gu Y , et al. Influence of solution PHvalue on structural properties of CdS thin films[J]. Journal of Optoelectronics Laser, 2013, 24(11):2169-

2173.
[7]Oliva A I , Corona J E , Pati?O R , et al. Chemical bath deposition of CdS thin films doped with Zn and Cu[J]. Bulletin of Materials ence, 2014, 37(2):247-255.
[8]Offiah S U, Agbogu A N C, Nwanya A C, et al. Influence of cadmium precursor concentrations on the structural, optical and electrochemical impedance properties of Cd1-xZnxS thin films[J]. Vacuum, 2019, 160: 246-254.
[9]Yao H , Shen H , Zhu X , et al. Influence of Cd source concentration on photo-current response property of CdxZn1-xS film prepared by chemical bath deposition[J]. Ceramics International, 2016, 42(2):2466-2471.
[10] Munna F T, Chelvanathan P, Sobayel K, et al. Effect of zinc doping on the optoelectronic properties of cadmium sulphide (CdS) thin films deposited by chemical bath deposition by utilising an alternative sulphur precursor[J]. Optik, 2020, 218: 165197.
[11] Carreón-Moncada I, González L A, Pech-Canul M I, et al. Cd1-xZnxS thin films with low Zn content obtained by an ammonia-free chemical bath deposition process[J]. Thin Solid Films, 2013, 548: 270-274.
[12] Liu J, Wei A, Zhao Y. Effect of different complexing agents on the properties of chemical-bath-deposited ZnS thin films[J]. Journal of alloys and compounds, 2014, 588: 228-234.
[13]Kaleli M . Effect of Sulphurization and Al Doping on Cd0.25Zn0.75S Thin Films Deposited by Ultrasonic Spray Pyrolysis Technique[J]. Optik - International Journal for Light and Electron Optics, 2019, 207:163781.
[14]Zhou Z , Guo L . Cd1-xZnxS energy band calculated by the first-principle method[J]. Hsi-An Chiao Tung Ta Hsueh/Journal of Xi'an Jiaotong University, 2008, 42(2):248-251.
[15]Salem A M . Structure, refractive-index dispersion and the optical absorption edge of chemically deposited ZnxCd(1-x)S thin films[J]. Applied Physics A, 2002, 74(2):205-211.