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Zinc Sulfide Buffer Layer for CIGS Solar Cells Prepared by Chemical Bath Deposition

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Abstract

In this study, ZnS thin films were successfully synthesized by chemical bath deposition (CBD) with starting materials of NH_2-NH_2, $SC(NH_2)_2$, and $ZnSO_4 \cdot 7H_2O$. ZnS thin films were deposited with different time on glass substrates by CBD at 80°C and pH=9. Based on X-ray diffraction (XRD) patterns, it is found that the ZnS thin films exhibit cubic polycrystalline phase. It was found that the optimum deposition time is 90 min for preparing ZnS thin film that is suitable as buffer layer for $CuIn_{1-x}Ga_xSe_2$ solar cells. The thin film deposited for 90 min has high transmittance up to 80% in the spectra range from 350 nm to 800 nm, and the optical band gap is about 3.59 eV.

Keywords: ZnS, buffer layer, chemical bath deposition, thin film solar cells, optical property

1. Introduction

Zinc sulfide is a wide-band-gap semi- conductor with a range of potential applications in optoelectronic devices. Generally, in thin film solar cells based on $CuInS_2$, $CuInSe_2$, $Cu(In,Ga)Se_2$, $Cu(In,Ga)(SSe)_2$, (CIGSSe), the buffer layer is mainly the II-VI type semiconductor, such as cadmium sulfide (CdS) and zinc sulfide (ZnS) thin film [1]. The buffer layer with II-VI type semiconductor is a direct gap semiconductor. The band gap of cadmium sulfide is 2.26~2.5 eV, and zinc sulfide is larger than 3.5 eV [2]. The highest efficiency is up to 19.9%, if the $CuIn_{1-x}Ga_xSe_2$ thin film solar cell combined with cadmium sulfide buffer layer at present [3]. For fear of cadmium (Cd) toxicity damages our environment, we have to choose a free-cadmium process for preparation of buffer layer. We utilize zinc sulfide as buffer layer and the efficiency of $CuIn_{1-x}Ga_xSe_2$ thin film solar cell with zinc sulfide buffer layer is up to 18.6% [4]. Consequently, there is no toxicity in the use of zinc sulfide and that can lower and lighten the influence on the environment.

The buffer layer located between ZnO windows layer (n-type semiconductor) and $CuIn_{1-x}Ga_xSe_2$ absorption layer (p-type semiconductor) is able to eliminate the band discontinuity. The ZnS buffer layer requires high optical transmission and allows photon to reach absorption layer to excite electron, and then electron-hole pairs (EHP) are generated. If the buffer layer is too thick, photoelectron can't pass through the layer and reach to electrodes. On the contrary, the layer is too thin that couldn't separate absorption layer and transition conduction electric layer (TCO). For better performance, the thickness of thin film should be controlled in the range of 30-50 nm.

Chemical bath deposition (CBD) method has been used for many years to prepare ZnS large-area and uniform thin film, and it can be prepared under room temperature [5]. Utilizing the CBD method produces nano-structure thin film of zinc sulfide with smooth surface and uniform composition, and it improves the efficiency of $CuIn_{1-x}Ga_xSe_2$ thin film solar cell. In this study, we attempt to prepare the uniform zinc sulfide thin film by CBD technique using NH3OH, NH2-NH2, SC(NH2)2, and $ZnSO_4 \cdot 7H_2O$ as starting materials, and investigate its characterizations such as structural, compositional and optical properties.

2. Method

In this study, ZnS thin film buffer layer prepared by chemical bath deposition process. Zinc sulfate ($ZnSO_4 \cdot 7H_2O$) and thiourea ($SC(NH_2)_2$) were used as the source of zinc ions and sulfide ions, respectively. The reaction so-

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lution was obtained by mixing 0.1M $ZnSO_4 \cdot 7H_2O$, 0.3M $SC(NH_2)_2$, and 1.5M N_2H_4, whereby hydrazine (N_2H_4) was used as a complex agent. The pH of the reaction solution was adjusted to 9 by ammonia (NH_3OH), reaction solution temperature was controlled at 80°C and the rotational speed of stirrer was controlled in 50 rpm. Soda-lime glass substrates were used as substrates for the deposition of ZnS films. Before deposition, the substrates were ultrasonically cleaned with acetone, rinsed with deionized water and dried in air. To investigate the effect of deposition time on properties of ZnS, the substrates were collected every 30 minutes in which the deposition-time is set in the range of 30 to 180 min. Then these samples were cleaned by deionized water and dried with a N_2 gas stream. In order to obtain crystalline ZnS, these as-deposited ZnS specimens required a post-annealing in a tube furnace for l h under Ar atmosphere at 300°C.

The average roughness of the ZnS films was investigated by surface profile measuring system (alpha-step, Veeco Dektak^{3}ST). The composition of ZnS thin films was analyzed by energy dispersive spectrometer (EDS, Horiba NORAN instrument). The crystalline phase of the annealed ZnS films were characterized by X-ray diffractometer (XRD, Rigaku D/ MAX-2500 V) with a wavelength of 1.5406Å from the CuKα radiation with 2θ ranging from 20° to 60°. Optical properties of thin films were characterized by an UV-vis spectrometer (Jasco V-650 spectrophotometer). The band gaps (E_g) of ZnS films were determined by the relationship of the transmittance and thickness of the film.

3. Results and Discussion

Fig. 1 shows X-rays diffraction of the zinc sulfide thin film annealed at 300°C for 1 h under argon atmosphere. ZnS exists with two structures, one is cubic with zinc-blende type the other is hexagonal with wurtzite type. ZnS thin films prepared via the chemical bath deposited are highly disordered, but it can be transformed into a wurtzite-2H phase by annealing [6]. Göde et al. reported that an amorphous ZnS film obtained at bath temperature of 60–70°C and a wurtzite-2H phase acquired at 80°C [7]. In this study, ZnS thin film prepared by CBD is zinc-blend type with cubic structure being in correspondence with JCPDS card no. 79-043. The XRD pattern reveals a wide diffraction peak from 25° to 30°. There are three diffraction peaks corresponding to (111), (220) and (311); however, the diffraction peaks in (200) and (311) are not clear indicating the zinc sulfide thin film with low crystallization.

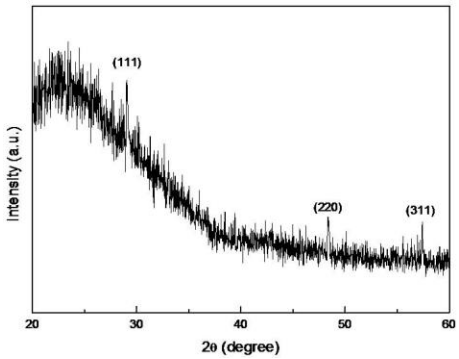

Fig. 1 X-rays diffraction pattern of ZnS thin film at deposition time of 90 min, then annealed at 300 °C for 1h under Ar atmosphere

To understand the effect of the deposition time on the composition of films, the energy dispersive spectrometer (EDS) was used to analyze the atomic ratio of Zn/S listed in Table 1. It is found that the ratio of Zn/S is close to 1 for films with various deposition times.

Table 1 The composition ratio of Zn/S at different deposited time

Composition	Deposition time (min)					
	30	60	90	120	150	180
Zn (Atom %)	50.4	51.9	50.3	51.2	50.8	49.8
S (Atom %)	49.6	48.1	49.7	48.8	49.2	50.2

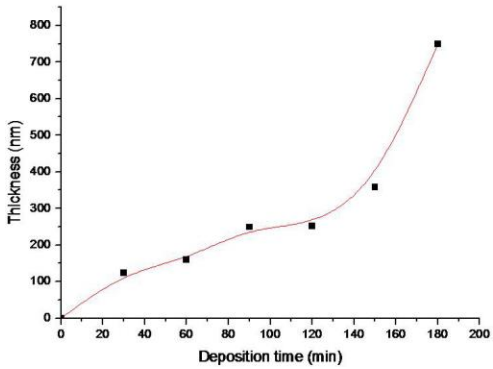

Fig. 2 The Thickness of ZnS films as a function of deposition time, after annealing at 300°C for 1 h under Ar atmosphere

Fig. 2 shows the ZnS film thickness as a function of deposition time. Apparently, the relation between thickness and deposition time is divided into two stages, the first stage is the linear growth for thin film and the thickness grows from 124 nm to 252 nm in the period of 30 ~ 120 min. However, the second stage is the exponential growth; the thickness significantly increases from 352 nm to 750 nm for deposition time from 120 to 180 min. At the second stage, the ZnS film undergoes homogeneous nucleation. As deposition time increasing above 150 min, homogeneous particles begin to deposit on the substrate leading the significant enhancement in growth rate of thin film. Table 2 is ZnS thin film thickness and roughness as function of deposition time. The average roughness of film for deposition time of 30 min is significantly high due to the facts that the heterogeneous deposition on substrate is still not uniform at the initial stage. As deposition time from 30 to 120 min, the roughness is relatively lower and the thin films become uniform gradually. When deposition time for 180 min, the rate of homogeneous deposition on substrate increased, and the average roughness of ZnS film is increased up to 94 nm.

Table 2 The thickness and average roughness for ZnS films with different deposition time

Deposition time (min)	30	60	90	120	150	180
Thickness (nm)	124	160	249	252	358	750
Average roughness (nm)	87	30	58	34	32	94

Fig. 3 shows the optical transmittance in the wavelength range of 300 - 800 nm for the ZnS films deposited on the sodium glass substrates as a function of different deposition time. The ZnS films reveled high optical transmittance in the range of 70 ~ 80% at visible wavelength; therefore, the films are suitable as buffer layers in CIGS-based solar cells. The highest transmittance of 85% is located about wavelength of 425 nm for deposition time of 90 min. As deposition time increased from 90 to 150 nm, the absorption edge shifted gradually from 400 nm to 500 nm. The sharp absorption feature is due to the uniform ZnS thin films and the low concentration of defects in the films. However, as the deposition time increased, thickness became thicker, and more homogeneous particles deposited on the glass substrate leading the optical transmittance lower than 80% for films that deposition time is above 90 min. Based on optical results, the film deposited for 90 min exhibited good optical properties, and the shortest wavelength of adsorption edge, which could make CIGS solar cell with a higher short circuit density (V_{sc}) [8].

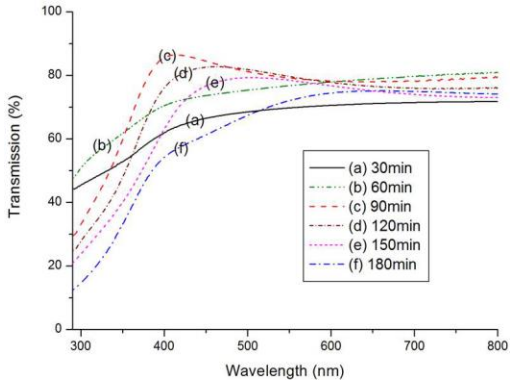

Fig. 3 Transmission spectra of ZnS thin films at different deposition time on glass substrates. Bath conditions: [$ZnSO_4$] =0.1M, [$SC(NH_4)$]=0.3M, [NH_2-NH_2]=1.5M, pH=9

The optical band gap of ZnS films could be obtained using the Tauc relationship revealed as follows [9].

$$\alpha h\nu = A(h\nu - E_g)^n \quad (1)$$

where A is a constant, h is Planck's constant, ν is the photon frequency, E_g is the optical band gap energy, and n is 1/2, respectively. The band gap value was determined from the intercept of the straight-line portion of the $(\alpha h\nu)^2$ against the graph on the hν-axis. The band gap values of the ZnS thin films prepared by CBD with various deposition time are revealed in Table 3. The band gap values are greater than 3.5 eV for the films deposited from 30 to 120 min. Higher band gap values could match well with CIGS solar cell, and the solar cells gain better quantum efficiency [10].

Table 3 The band gap for ZnS thin films with various deposition time

Deposition time (min)	30	60	90	120	150	180
Band gap (eV)	2.57	3.53	3.59	3.54	3.45	3.30

4. Conclusions

In this study, the ZnS thin films with sphalerite structure prepared by chemical bath deposition using zinc sulfate, thiourea, and complex of hydrazine as starting materials. The thickness of ZnS thin film varies with deposition time from 124 nm of 30 min to 750 nm of 180 min. The ZnS films reveled high optical transmittance in the range of 70 ~ 80% at visible wavelength. The band gap values for ZnS films are in the range of 2.57 ~ 3.61 eV. Based on the results, the following bath conditions, [ZnSO4]=0.1M, [SC(NH4)]=0.3M,
[NH2-NH2]

[=1.5M, pH=9 and T=80^{o}C deposited for 90 min, revealed the optimum ZnS film properties, which is suitable as buffer layer for $CuIn_{1-x}Ga_xSe_2$ solar cells, and the properties of the film are described as follows. (1). XRD pattern reveals a cubic zinc blend structure with the typical composition ratio of Zn/S = 50.3:49.7, which is very close to the stoichiometry of the ZnS compound. (2). The highest transmittance of 85% is located about wavelength of 425 nm and the optical band gap is about 3.59 eV.

References

[1] A. Wei, J. Liu, M. Zhuang, and Y. Zhao, "Preparation and characterization of ZnS thin films prepared by chemical bath deposition," Materials Science in Semiconductor Processing, vol. 16, pp. 1478-1484, December 2013.

[2] B. G. Streetman and S. K. Banerjee, "Solid state electron devices," 6th edition, Pearson Prentice Hall, New Jersey, pp. 158-208, 2006.

[3] I. Repins, M. A. Contreras, B. Egaas, C. DeHart, J. Scharf, C. L. Perkins, B. To, and R. Noufi, "Accelerated publication 19.9%-efficient ZnO/CdS/$CuInGaSe_2$ solar cell with 81.2% fill factor," Progress in Photovoltaics: Research and Applications 16, pp. 235, 2008.

[4] R. N. Bhattacharya and K. Ramanathan, "Cu (In,Ga)Se_2 thin film solar cells with buffer layer alternative to CdS," Solar Energy, vol. 77, pp. 679-683, 2004.

[5] J. Liu, A. Wei, and Y. Zhao, "Effect of different complexing agents on the properties of chemical-bath-deposited ZnS thin films," J. Alloys Compd., vol. 588, pp. 228-234, 2014.

[6] I. O. Oladeji and L. Chow, "Synthesis and processing of CdS/ZnS multilayer films for solar cell application," Thin Solid Films, vol. 474, pp. 77-83, 2005.

[7] F. Göde, C. Umus, and M. Zor, "Investigations on the physical properties of the polycrystalline ZnS thin films deposited by the chemical bath deposition method," J. Cryst. Growth, vol. 299, pp. 136-141, 2007.

[8] S. W. Shin, S. R. Kang, K. V. Gurav, J. H. Yun, J. H. Moon, J. Y. Lee, and J. H. Kim, "A study on the improved growth rate and morphology of chemically deposited ZnS thin film buffer layer for thin film solar cells in acidic medium," Solar Energy, vol. 85, pp. 2903-2911, 2011.

[9] S. W. Shin, G. L. Agawane, M. G. Gang, A. V. Moholkar, J. H. Moon, J. H. Kim, and J. Y. Lee, "Preparation and characteristics of chemical bath deposited ZnS thin films: Effects of different complexing agents," J. Alloys Compd., vol. 526, pp. 25-30, 2012.

[10] R. N. Bhattacharya, K. Ramanathan, L. Gedvilas, and B. Keyes "Cu(In,Ga)Se_2 thin-film solar cells with ZnS(O,OH), Zn–Cd–S(O,OH), and CdS buffer layers," J. Phys. Chem. Solids, vol. 66, pp. 1862-1864, 2005.