Effect of sulfurization temperature on optical and compositional properties of sputtered Zn(O,S) thin films

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Abstract

Zinc oxysulfide or Zn(O,S) is emerging as an alternate n-type buffer layer for kesterite, chalcogenides and CdTe based thin film solar cell due to it is being made from non-toxic elements and tunable bandgap, its suitable optical and electrical properties required for a buffer layer. Generally, buffer layers of these solar cells are deposited using chemical bath deposition (CBD) techniques, but these require breaking of vacuum and again inserting the sample in vacuum during solar cell fabrication, which is not economical and is cumbersome. Sputtering is considered to be industrial process and therefore, here we have deposited Zn(O,S) thin film by sputtering technique and effect of sulfurization temperature on bandgap and composition of Zn(O,S) films have been studied. The bandgap of deposited films changed from 3.36 eV to 3.15 eV by changing the sulfurization temperatures. By changing the sulfurization temperature, the composition of films also changed. Crystallite size (D) of Zn(O,S) films increased from 12.1 nm to 22.3 nm by varying the sulfur content for samples S1-S4, respectively. Optical, morphological, compositional and structural properties have been studied using UV-Vis-NIR spectroscopy, Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDS) and X-ray diffractometer (XRD), respectively. Copyright © 2018 VBRI Press.

Keywords: Zn(O,S) films, Cd-free buffer layer, bandgap, sputtering, sulfurization/annealing.

Introduction

CuInGaSe$_2$ (CIGS) and CdTe based photovoltaics have already demonstrated 22.6% and 22.1% efficiency at laboratory scale, using CdS as n-type buffer layer [1-2]. CdS as buffer layer faces two issues. First is its toxicity which is related to the environmental safety and health issues [3-5]. Another is associated with its relatively smaller bandgap (2.4 eV), resulting in considerable amount of photon loss. Therefore, researchers are looking for an alternate Cd-free buffer layer with similar properties as CdS but made of earth abundant and environment-friendly elements and higher band gap. If the CdS can be replaced by higher bandgap materials, absorption loss can be minimized which would lead to improved solar cell efficiency. A buffer layer should have high transparency for incident light, good conduction band lineup with absorber material, low interface recombination, high resistivity and good device stability [6-7]. Zn(O,S) is being researched as a alternate n-type buffer layer because of its properties like made up of earth abundant, eco-friendly, non-toxic material and tunable bandgap from ~3.1 eV to ~3.6 eV [8-10]. Zn(O,S) film as n-type buffer layer

has high transparency to light in blue wavelength range, providing more sunlight to absorber materials, which then converts more light energy into electricity.

Zn(O,S) thin films can be prepared by different techniques like CBD, spray pyrolysis, atomic layer deposition (ALD) and sputtering [11-14]. The problem with liquid based (spray pyrolysis, CBD) technique was wastage of high amount of liquid and these are not suitable for mass production. Also, making buffer layer by chemical method require breaking of vacuum for removing and inserting the samples which is not only cumbersome and costly but also is a time consuming process. CIGS and CZTS absorber thin films have been already deposited and conditions for various applications have been optimized [15-20]. As CIGS based thin film solar cells with high efficiency using sputtering technique have already been commercialized, therefore, sputtered Zn(O,S) thin films as buffer layer would be compatible with CIGS and CZTS based solar cells processes. In this study, Zn(O,S) films with controlled composition have been deposited using three step process: DC sputtering method followed by annealing/sulfurization. The effect of sulfurization

temperature on the optical, structural and compositional properties of Zn(O,S) films have been studied. The main advantage of this technique is controlled substitution of sulfur even at higher temperature with good crystallinity of Zn(O,S) film.

Experimental details

Zn(O,S) films were prepared in three steps. In the first step, Zn thin film has been deposited by sputtering Zn metallic targets with 99.995% purity using DC sputtering onto quartz substrate at room temperature. In the second step, Zn films were kept in a horizontal sliding tube furnace for oxidation (for making ZnO film). Zn films were annealed in oxygen atmosphere (open air) at 500°C for 3 hrs and then cooled naturally to room temperature for obtaining ZnO films. In the third step, ZnO films were sulfurized in tube furnace in N_2 atmosphere. ZnO films were kept in graphite box containing sulfur powder (100 mg) and inserted into the horizontal tube furnace. The sulfurization process was carried out at various temperatures of 400°C, 500°C and 550°C for 2 hrs. After completion of sulfurization, samples were pulled out from hot zone to room temperature zone and allowed to cool down naturally. Thickness of deposited Zn(O,S) films estimated by stylus profilometer were ~360 nm. The detailed of each samples are shown in **Table 1**.

Table 1. Details of sample deposition.

Sample	Description	Oxidation Condition		Sulfurization Condition	
		Temperature (°C)	Time (hrs)	Temperature (°C)	Time (hrs)
S1	ZnO	500	3	-	-
S2	Zn(O,S)	500	3	400	2
S3	Zn(O,S)	500	3	500	2
S4	Zn(O,S)	500	3	550	2

The structure properties of ZnO and Zn(O,S) films were investigated using Cu-Kα radiation of X-ray diffractometer (XRD) operating at λ = 1.54056 Å, 40 kV and 20 mA (Philips X'pert pro X-ray diffractometer). Optical properties were studied using UV-Vis-NIR spectrophotometer (Shimadzu UV-1800) in the wavelength range of 300 nm to 1800 nm. The compositional analysis and surface morphologies were studied using the Energy Dispersive X-ray Spectroscopy (EDS) and Scanning Electron Microscope (SEM) with (Zeiss EVO-50), respectively. EDS was attached with SEM.

Results and discussion

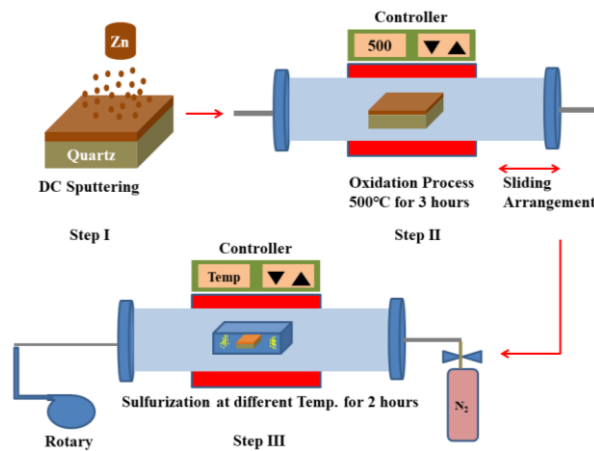The schematic of deposition of ZnO and Zn(O,S) films using sputtering technique in three steps is shown in **Fig.1**.

Fig.1. Schematic of Zn(O,S) thin film deposition.

Fig. 2 represents the Tauc plot between $(\alpha h\nu)^2$ and $h\nu$ for samples S1, S2 S3 and S4, respectively. For direct bandgap semiconductors, the bandgap (E_g) of any materials can be estimated using following formula: $(\alpha h\nu)^2 = A(h\nu - E_g)$, where α is the absorption coefficient, $h\nu$ is the photon energy and A is a constant. The estimated bandgap for samples S1, S2, S3 and S4 are 3.36 eV, 3.22 eV, 3.17 eV and 3.15 eV, respectively. From Table 3 it is clear that bandgap decreases from sample S1-S4 from 3.36 eV to 3.15 eV after sulfurization at various temperatures due to increase in sulfur amount from 0 to 22.3 at% for samples S2-S4. Incorporation of sulfur in ZnO structure strongly increases the valence band maximum (VBM) levels which results in decrease in bandgap of Zn(O,S) films [21-24].
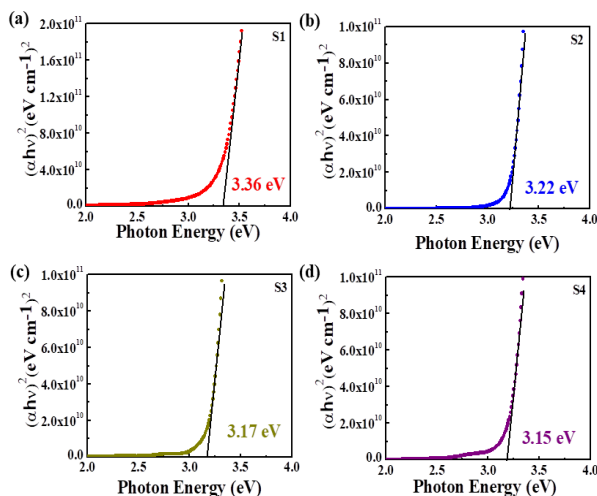

Fig. 2. Tauc plot of samples S1, S2, S3 and S4, respectively.

The elemental compositions were estimated using Energy Dispersive X-ray spectroscopy (EDS) and are presented in **Table 2**. The elemental compositions of deposited thin film samples (S1-S4) are similar to previously reported values [7, 13]. Samples S2-S4 reveals that sulfurization temperature plays crucial role in optimizing the quality of Zn(O,S) thin films.

Table 2. Elemental compositional analysis of ZnO and Zn(O,S) thin films.

Sample	Zn (at.%)	O (at.%)	S (at.%)	S/(S+O)
S1	52.7	47.3	0	0
S2	51.2	35.9	12.9	0.26
S3	50.8	31.8	17.4	0.35
S4	49.2	28.5	22.3	0.44

Fig. 3. (a-d) represents the surface morphology of samples S1, S2, S3 and S4, respectively. From SEM image it is clear that Zn(O,S) films are uniform in all samples S1-S3 but some structures were seen in sample S4 which may be due to access amount of sulfur content.
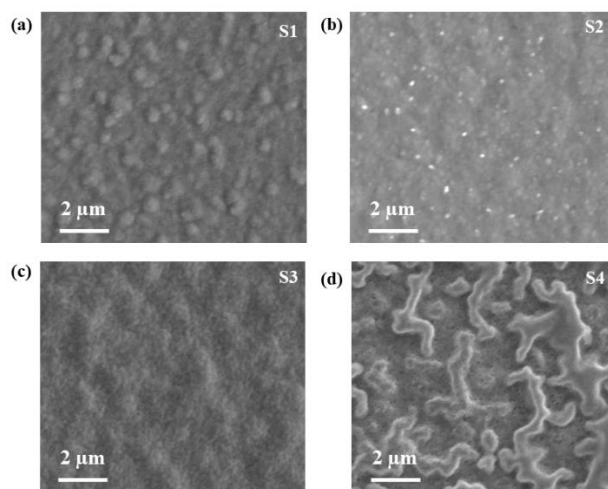
Fig. 3. Morphology of ZnO and Zn(O,S) thin films.

The crystallite sizes (D) for samples S1 to S4 were calculated using Scherer formula: $D = \frac{K\lambda}{\beta cos\theta}$, where D is crystallite size (nm), K is scherrer constant (0.9), λ is X-ray wavelength for CuKα (1.54178 Å), β is Full width at half maximum (FWHM) of XRD peak and θ is peak position one half of 2θ [25]. The calculated values of crystallite size (D) for peak (002) for all the samples are given in **Table 3**. Sample S3 have very good crystallite size which is required as n-type buffer layer for thin film based solar cells. It is clear that crystallinity improves and bandgap reduces with increase in sulfurization temperature.

Table 3. Effect of sulfurization temperature on crystallite size and band gap of sample S1-S4.

Sample	Peak	FWHM	D (nm)	Optical bandgap (eV)
S1	(002)	0.72	12.1	3.36
S2	(002)	0.45	19.3	3.22
S3	(002)	0.41	21.7	3.17
S4	(002)	0.39	22.3	3.15

Apart from ZnO pattern, (002) plane of ZnS wurtzite phase were observed for Zn(S,O) films as presented in **Fig. 4** (JCPDS Card No. 77-2100). The peak intensity of (002) plan is related to amount of sulfur content. With increase in the sulfur content, amount of ZnS phase in Zn(O,S) is increases [6-7, 11]. EDS results presented in **Table 2** also confirms this.

Fig.4. (a-d) represents the XRD spectra of samples S1, S2, S3 and S4, respectively.
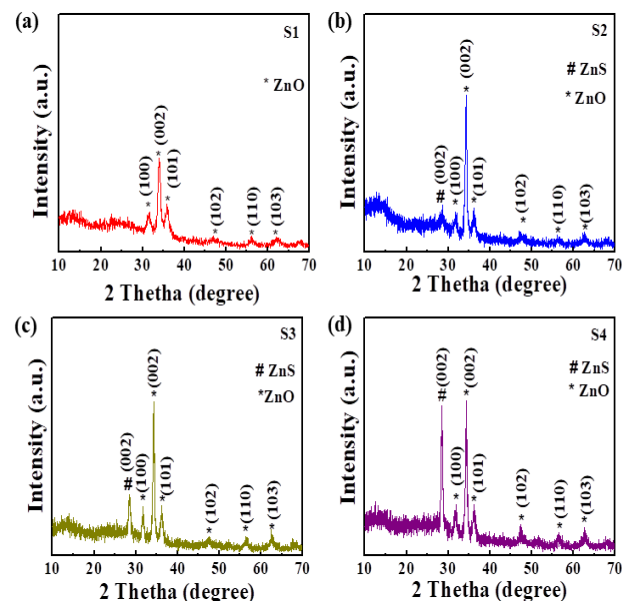

Fig. 4. XRD spectra for samples S1, S2, S3 and S4, respectively.

Fig. 5. (a) represents the optical transmittance spectrum in the range of 300-1800 nm for ZnO and Zn(S,O) films. The average optical transmittance of samples S1, S2, S3 and S4 are 65%, 90%, 87% and 75%, respectively. Of all the samples, S3 has very good transmittance (87%) which is good for n-type buffer layer for thin film solar cells. The transmittance values are comparable to previously reported values [6, 11, 26]. **Fig. 5. (b)** represents the effect of sulfurization temperature on the bandgap of sputtered Zn(O,S) films. **Fig. 5. (c)** represents optical absorbance spectrum. The bandgap of Zn(O,S) films get reduced by increasing the sulfurization temperature. The optical transmittance intensity is related to the structural properties and crystallinity of the samples. From absorption spectrum we can say that absorption edges of samples (S2-S4) shifts from shorter to longer wavelengths by increasing the amount of sulfur which leads to decrease in the bandgap of the deposited films. The improvement in the crystallinity will lead to decreased defects in the material which also leads to reduction in concentration of grain boundaries. This will result in decrease in optical absorption due to reduced scattering leading to high optical transmittance of Zn(O,S) film [27]. **Fig. 5. (d)** represents dependence of band gap on sulfur contents in Zn(S,O) thin films.
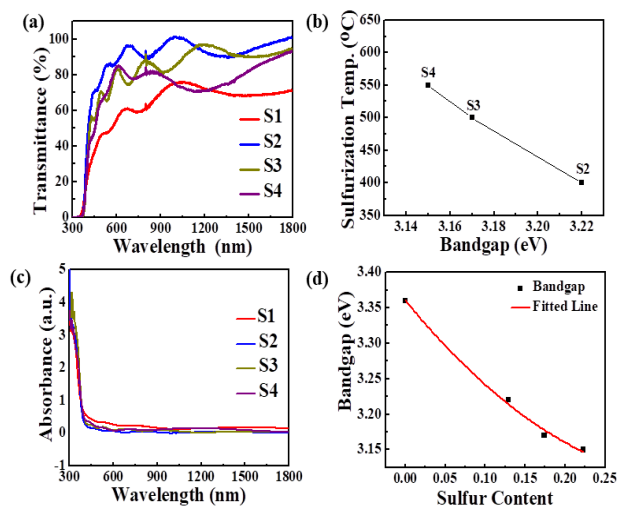
Fig. 5. (a) Optical transmittance spectrum. (b) Effect of sulfurization temp on bandgap. (c) Optical absorbance spectrum. (d) Bandgap energy as a function of sulfur contents.

In semiconductor alloys, the lattice parameter of material obeys a linear relationship between the band gap and compositions of alloys, Vegard's law can be used to calculate bowing parameter by using following [28-29].

$$E_g(x) = xE_g^{ZnS} + (1-x)E_g^{ZnO} - bx(1-x) \ \dots (1)$$

Where E_g^{ZnS} and E_g^{ZnO} are the bandgap of ZnS (3.55 ± 0.05 eV) and ZnO (3.31 ± 0.05 eV), respectively [21]. Where, x and b are the sulfur content and bowing parameter, respectively. By using nonlinear curve fitting, the estimated value of bowing parameter is 1.90 eV. This estimated value is smaller than values reported by *J. Jiang* (2.13 eV), *C. Persson* (3.0 eV) and *B.K. Meyer* (3.0 eV), respectively [9, 21, 29]. The optical bowing parameter of alloys is intensely associated to stoichiometry of the deposited films, which mainly depends on synthesis techniques. This difference in our value and reported values might be due to the difference in growth techniques of films.

This study helps in optimizing the optical and compositional properties of Zn(O,S) n-type buffer layer. It is clear that Zn(O,S) films as buffer layer have a huge scope in photovoltaic applications because it can overcome problems faced by other used buffer layer (CdS, In_2S_3 etc). The main problem associated with CdS n-type buffer layer is bandgap i.e. 2.4 eV and its toxicity [3, 30]. In In_2S_3 buffer layer, availability and cost of Indium (In) is major concern [31]. Due to low band gap if CdS, photons having wavelength shorter than 515 nm are absorbed in CdS film while in case of Zn(S,O) films, photon with around 400 nm wavelength can be transmitted, which would results in enhanced efficiency of thin film solar cells based on Zn(O,S) buffer layers. Tunable bandgap of Zn(S,O) films is an important parameter which can be utilized to optimize the band alignment in the hetero-junctions based solar cells. *K.S. Gour et al.* demonstrated CZTS and

$Cu_2ZnSn(S,Se)_4$ (CZTSSe) based photodetector for broadband and visible range [32-33]. *O.P. Singh et al.* studied petal type CZTS thin film and effect of Zn sputtered film thickness and annealing time on CZTS thin film as absorber materials [34-35]. Recently, *T. Taskesen et al.* reported 11.4% efficiency for $Cu_2ZnSnSe_4$ (CZTSe) solar cells using sputtering technique [36]. Thus, Zn(O,S) thin film can also be used in CZTS, CZTSe based thin film solar cells and hetero-junctions based thin film photodetection applications.

Conclusion

Here, we studied the effect of sulfurization temperature on optical and compositional properties of sputtered Zn(O,S) thin films. It is confirmed that optical properties of Zn(O,S) films intensely depend upon sulfurization temperature which influences the composition, morphology and structure of films. Sample S3 sulfurized at 500°C shows very good transmittance value of about 87% and bandgap of 3.17 eV. Sample S3 also have good crystallite size (D) of 21.7 nm. Thus, among all the four samples, sample S3 has better optical, structural, morphological and compositional properties. These properties makes Zn(O,S) thin film a strong candidate as n-type buffer layer to enhance the overall efficiency of CIGS and CZTS based thin film solar cells. Therefore Cd-free Zn(O,S) buffer layers can be utilized as n-type layer for solar cells and also can be utilized in photodetector applications.

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Highlights

- Zn(O,S) thin films have been deposited by DC sputtering technique of Zn and further oxidation/sulfurization.
- Optical bandgap and transmittance of optimized Zn(O,S) film were 3.17 eV and ~87%, respectively which is good for a buffer layer.
- Zn(S,O) films can overcome difficulties faced by the most used buffer layer (CdS, In_2S_3 etc.).
- The present method is an industrially viable technique to deposit Zn(O,S) thin films for solar cell applications.