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Effect of dopent on the structural and optical properties of ZnS Thin Film as a buffer layer in solar cell application

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Abstract: In order to find the suitable alternative of toxic CdS buffer layer, deposition of pure ZnS and doped with Al by chemical bath deposition method have been reported. Further as grown pure and doped thin films have been annealed at 150^0C. The structural and surface morphological properties have been characterized by X-Ray diffraction (XRD) and Atomic Force Microscope (AFM).The XRD analysis shows that annealed thin film has been polycrystalline in nature with sphalerite cubic crystal structure and AFM images indicate increment in grain size as well as growth of crystals after annealing. Optical measurement data give band gap of 3.5 eV which is ideal band gap for buffer layer for solar cell suggesting that the obtained ZnS buffer layer is suitable in a low-cost solar cell.

1. INTRODUCTION

Buffer layer play a vital role in thin film heterojunction solar cell by formation of junction with the absorber layer for transporting photo generated charge carriers to the load as well as admitting maximum amount of solar light to the absorber layer. For solving this purpose material with high band gap and low resistivity is required. CdS is most commonly used material for buffer layer deposited by Chemical Bath Deposition (CBD) technique [1-2]. Although in most laboratories standard device structure use buffer layer of CdS in solar cell, but meanwhile in last decade risk assessment arise from toxicity of CdS leads researchers to other nontoxic n-type materials with low cost deposition technique. In this context films based on ZnS, ZnSe, ZnO were deposited as an alternative to the CdS buffer layer, among them ZnS is one of the most popular candidates. ZnS based thin films have advantage of less toxicity and high energy band gap (3.54 eV) which fulfill the requirement of maximum solar energy availability for absorber layer. However, doping of high conductivity elements such as Al, Cu, and Ni gives the possibility of decrement in electrical resistivity without affecting the optical properties of the layers [3-4].

There are several methods have been used to deposit this n-type material based on PVD and CVD, among them Chemical Bath Deposition (CBD) method is interesting one because it is simple, reproducible, non-hazardous, cost effective and well suited for producing large-area thin films at low temperatures[5-7]. So, the central theme of this work is optimizing and controlling of synthesis parameters for pure and doped ZnS thin films and comparative study of the effect of doping on the properties of the deposited films. Further post treatment thermal annealing has used as it can control the morphology and structural properties of polycrystalline thin film. Considering this aspect we studied the annealing effect on the ZnS thin films. Different characterization has done by different characterization tools for as deposited and annealed ZnS thin film.

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2. EXPERIMENTAL

2.1 Deposition of ZnS Thin Film: All the chemicals used for preparation of chemical bath were analytical reagent grade (AR) provided by Sigma Aldrich with 99.9% purity. Zinc Sulfate heptahydrate ($ZnSO_4.7H_2O$) and Thiourea (NH_2CSNH_2) were used as precursor chemicals for Zn^{2+} and S^{2-} ions for pure ZnS thin film and Aluminum Sulfate 16-hydrate ($Al_2(SO_4)_3.16H_2O$) was used for doping ion Al^{+2}, Hydrazine Hydrate and TEA was used as complexing agent for controlling the reaction mechanism. Thin films were deposited on Soda Lime Glass (SLG). Before the deposition, substrates were cleaned by detergent and distilled water then ultrasonically cleaned by Acetone, Methanol and De-ionized (DI) water and dried in air.

Chemical concentrations were taken as 0.1 M $ZnSO_4$, 0.1 NH_2CSNH_2 in equal volume ratio and Hydrazine Hydrate and TEA were taken as complexing agent. Initially solution was prepared by dissolving chemicals in distilled water by magnetic stirring separately. After preparing all the solutions they were mixed and final pH (~12) was controlled by adding Sodium Hydroxide solution. Cleaned SLG substrate was immersed in the solution and solution was heated up to 80^{o}C. Schematic diagram for the deposition is shown in Fig. 1. After 10 min. precipitation started to form in the bath and deposition of ZnS film started on the substrates. After 2 hr ZnS film was deposited on substrate.

For deposition of doped ZnS thin film 0.1 M $ZnSO_4$, 0.01 M $Al_2(SO_4)_3$ and 0.1 NH_2CSNH_2 was taken in equal volume ratio. Same procedure was followed for deposition of doped film. After 2 hr doped ZnS film was deposited on substrate. Deposited films were removed, rinsed in DI water to remove the ions from film, dried in air and preserved in desiccator.

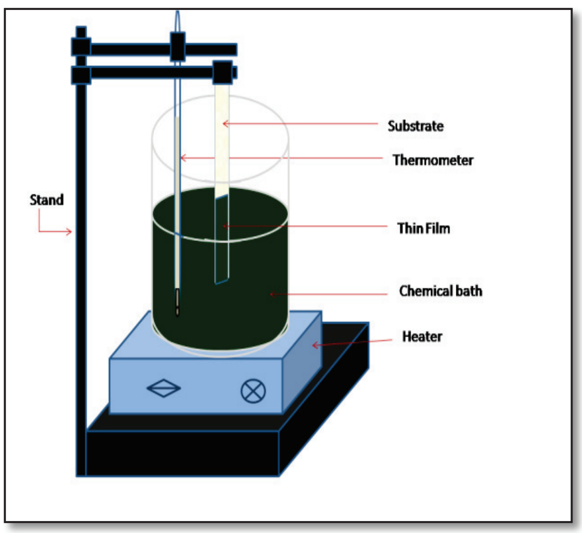

FIGURE 1. Schematic diagram of chemical bath deposition method for deposition of ZnS thin films.

The surface of the thin film can be modified by providing the post deposition treatments like thermal annealing. So, as deposited and doped ZnS thin films were annealed in air at 150^{0}C for 2 hr in tubular furnace.

2.2 Characterization: The structural properties of as deposited and annealed CZTS thin film were studied by X-ray diffraction (XRD) pattern by using PANalytical X'Pert Pro X-ray Diffraction Unit with copper (Cu), which have strong Kα radiation having X-ray emissions wavelength of 1.5418 Å in range of 20-60o. Average crystal sizes were determined according to broadening of peaks using Scherrer relationship. The surface morphological study was carried out using Atomic Force Microscope (AFM).U-V characteristic studied using LAMBDA 950 UV/Vis/NIR Spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Structural Analysis

X-ray diffraction (XRD) technique was used for performing structural analysis of as-deposited, annealed thin films on glass substrate. Fig. 2 shows the XRD pattern of as deposited and annealed pure and doped ZnS film. Fig. 2(A) shows no diffraction peaks indicating amorphous nature of as deposited film. Fig. 2[B(a)] shows XRD pattern of annealed pure ZnS film at 150^0C for 2 hr. and exhibit sharp peaks at different angles 28.55, 33.20 and by comparing calculated 'd' values with experimental 'd' values of standard sphalerite structured ZnS crystal(JCPDS card 05-0566), corresponding phases can be determined Which are (111),(200). Fig. 2[B(b)] shows XRD pattern of annealed doped ZnS film at 150^0C for 2 hr. which gives sharp peaks at angles 28.55, 33.20, 47.48 and 56.50 and by comparing standard sphalerite structured corresponding phases can be determined Which are (111),(200),(220) and (311). This analysis conform the synthesis of sphalerite cubic structured ZnS thin film. This result is in agreement with previously reported results [8-9]. Intensity of peak corresponding (111) phase is observed to be much greater than other peaks, reveling preferred orientation along this phase for annealed film.

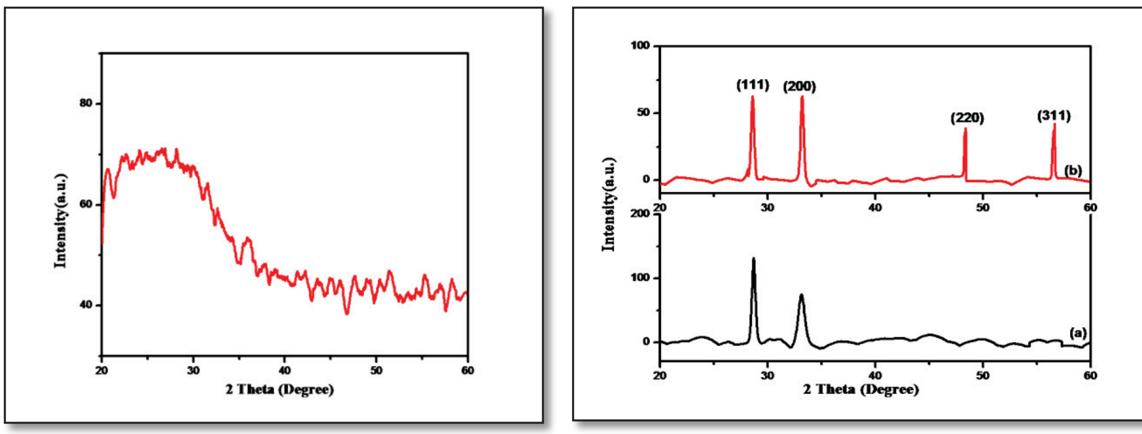

FIGURE 2(A). XRD patterns of as deposited ZnS thin film **2(B)** XRD patterns of (a) annealed pure ZnS and (b) annealed doped ZnS thin film at 150^o C in air for 2 hr.

Particle size in the doped film was calculated from the Scherrer's formula

$$D = \frac{0.9\lambda}{\beta Cos\theta} \quad (1)$$

Where λ is X-ray wavelength, β is the full width at half maximum (FWHM) in radians, and θ is the Bragg angle. FWHM of diffraction peaks and grain size and other parameters for doped film are shown in Table (1).

Table1. Parameters of XRD spectra for ZnS thin films

2 Theta (degree)	d(Å)	Intensity	hkl	FWHM	Grain Size (nm)
28.55	3.36	100	111	0.322	26.53
33.60	2.69	10	200	0.324	26.73
47.48	1.91	51	220	0.227	39.95
56.50	1.62	30	311	0.197	47.83

3.2Surface morphological analysis

Surface morphological analysis was done by Atomic Force Microscope (AFM). Fig. 3 shows 2D AFM image of as-deposited and annealed pure and doped ZnS thin film taken over 3μm^2 area. Fig. 3(a) shows AFM image of as-deposited film indicate the homogenous background with smaller densely packed grains. It was observed that some particles exist on the surface of film which may be because during deposition process nucleation sites was developed. After annealing in pure ZnS film grain growth started and spherical grains have been found [Fig. 3(b)].

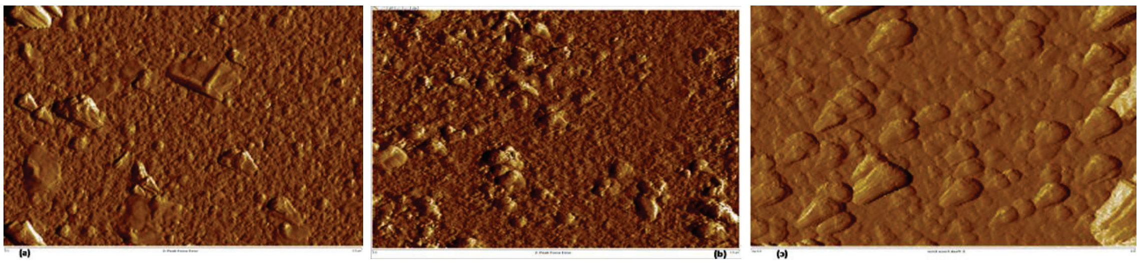

FIGURE 3. The 2D AFM images of (a) as deposited and (b) annealed pure ZnS (c) annealed doped ZnS thin film at 150^o C in air for 2 hr.

Fig. 3(c) shows surface image of doped annealed film and indicates surface modification occur after post temperature treatment which increase crystallinity and grain size of thin film. These large grains are useful for solar cell application because it reduce localized recombination sources [10]. Average surface roughness of as deposited and annealed pure and doped ZnS films are 12.7, 33.7 and 92.1nm respectively and root mean square roughness are 8.74, 17.5 and 58.5 respectively.

3.3 Optical absorption Study

In order to study absorption spectra and energy band gap of ZnS thin film the optical absorption has been studied in the wavelength range 800 nm to 300 nm. In Fig. 4(A) variation of absorbance (a. u.) with respect to wavelength (λ) shows that ZnS films have high absorbance in ultraviolet region. Further optical data were analyzed by using Tauc relation [11] from which the absorption coefficient α, for semiconductor material is given by

$$\alpha = \frac{A(h\upsilon - Eg)^n}{h\upsilon} \qquad (2)$$

Where α is absorption coefficient, A is constant, $h\upsilon$ is incident photon energy, Eg is energy band gap, n is constant which depends on the nature of transition i.e. n=1/2 for allowed direct transition, n=2 for allowed indirect transition. Plot of (αhυ)2 (by taking n=1/2) vs hυ is a straight line which show it is a direct band gap material.

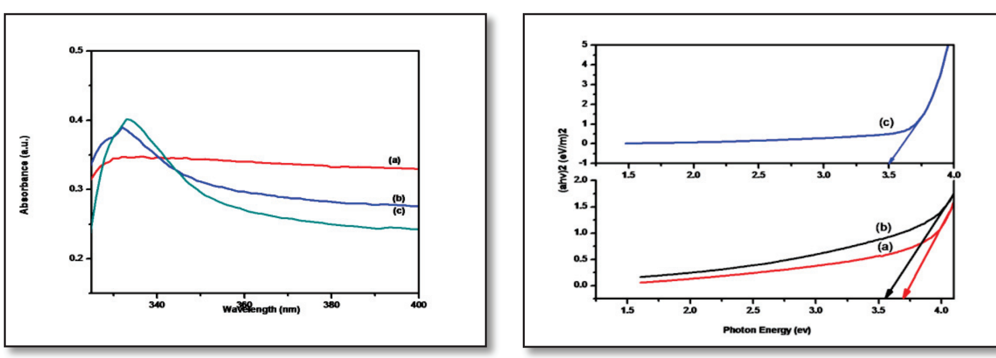

FIGURE 4(A). Variation of absorption (a.u.) with wavelength (nm) of (a) as deposited and (b) annealed pure ZnS (c) annealed doped ZnS thin film at 150^o C in air for 2 hr. **4(B)** The plots of $(\alpha h\upsilon)^2$ vs hυ of (a) as deposited and (b) annealed pure ZnS (c) annealed doped ZnS thin film at 150^o C in air for 2 hr.

Extrapolation of Tauc plot to zero absorption coefficient (α=0) give energy band gap values. Fig. 4(B) shows that band gap energy decrease from 3.69 eV (fig 4B, a) to 3.56 eV (fig 4B, b) with increase in annealing temp for pure ZnS thin film. Energy band gap for doped annealed ZnS thin film is 3.5 eV (fig 4B, c).So calculated band gap energy values are in good agreement with reported data [12-13]

4. CONCLUSION

ZnS thin film buffer layer by low cost Chemical Bath Deposition (CBD) technique was synthesized by optimizing parameters. Conclusively, deposition temperature of 80^0C and deposition time of 2 hr reported for synthesis of ZnS thin film. For improving the properties of as deposited film annealing was performed. As deposited and annealed thin films were characterized by different characterization tools. Surface morphology of CZTS film shows increase in grain size with annealing temperature increases and a direct optical band gap energy of 3.5 eV.

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