STUDY OF CHEMICAL BATH DEPOSITED NANOCRYSTALLINE CdZnS THIN FILMS

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In this paper we report the study of $Cd_{1-x}Zn_xS$ thin films grown on commercial glass slide substrate by chemical bath deposition technique at 70±2ºC. The effect of zinc content (x value) on structural, morphological and some optical properties have been studied. The as-deposited $Cd_{1-x}Zn_xS$ thin films were characterized using X-ray diffractometer (X-PERT PRO), SEM and UV-VIS spectrophotometer. All the films show nanocrystallinity with both cubic and hexagonal structure. The average grain size changes from 8.75nm to 3.57nm with increase in zinc content. It was found that as the zinc content increases, the peak intensity decreases and for $x \geq 0.8$ the films have near amorphous character. The values of energy bandgap obtained are between 2.48 eV and 3.62 eV for Zn content between 0 and 0.8 respectively. The other optical properties were under consideration.

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1. Introduction

Cadmium zinc sulfides $Cd_{1-x}Zn_xS$ have properties in between CdS and ZnS. Addition of Zn to the most widely used CdS buffer layer material enhances the electronic and optical properties of optoelectronic devices. The CdZnS thin film band structure has a larger energy gap than CdS. This makes the material much more attractive for the fabrication of solar cells. It has been widely used as a wide bandgap window material in hetero-junction photovoltaic solar cells and photoconductive devices. Keeping these aspects in view, more attention is being given in producing good quality CdZnS thin films for comprehensive optical studies and their various applications.

A number of film deposition methods such as spray pyrolysis, sputtering, electro deposition, vacuum evaporation, chemical vapour deposition and chemical bath deposition (CBD) have been used for preparing II-VI compounds.[1-4]

In this study, we were prepared the $Cd_{1-x}Zn_xS$ thin films for varying Zn content by a modified CBD technique. The effects of Zn content on structural, morphological and some optical properties have been investigated.

2. Experimental details

The $Cd_{1-x}Zn_xS$ thin films were prepared by CBD technique on commercial glass slide for various zinc concentration (x= 0, 0.2, ….., 0.8). The starting materials used were $CdSO_4$ (0.06M) as a Cd^{2+} ion source, $ZnSO_4$ (0.2M) as Zn^{2+} ion source, thiourea (0.6M) as an S^{2-} ion source and triethenolamine (TEA) complexing to control the Cd^{2+} and Zn^{2+} ion concentrations. An alkaline solution of ammonia was used to adjust pH of the reaction mixture. All the chemicals used were of Analytical Reagent grade. The process involving a controllable chemical reaction at a low rate, by

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adjusting the pH value and temperature of the working solution allows maintaining the stoichiometry constant for any ratio of anions and cations. The experimental arrangement consists of a special substrate holder which is attached to a motor having a constant speed of 60 r.p.m. The temperature of chemical bath was adjusted with a hot plate and temperature controller (72±2ºC), while magnetic stirrer is applied to promote ion-by-ion heterogeneous growth on the substrate. The $Cd_{1-x}Zn_xS$ samples were prepared on carefully cleaned glass substrates. Cleaning of substrate is important in deposition of thin films, cleaning steps and growth procedure is reported elsewhere [6, 8]. The pH value of working solution was adjusted by a pH meter and kept in between 9 and 9.5 for different deposition time (10-60min.). After deposition the substrates were removed from the chemical bath and cleaned in double distilled water.

The crystallographic structure of the films was analyzed with a (XPERT-PRO) X-ray diffractometer using Cu-Kα radiation with wavelength, 1.5418Å. The thickness of thin film was measured by the weight difference method at room temperature.

The average grain size in the deposited films was obtained from a Debye-Scherrer formula. Surface morphology was examined by JEOL model JSM-6400 scanning electron microscope (SEM). Optical properties were measured at room temperature by using Perklin-Elmer UV-VIS lambda-35 spectrometer in the wavelength range 200-1000nm.

3. Results and discussion

The films obtained were smooth, uniform, adherent, bright yellow orange in color and yellowness increases with increasing Zn content. Table 1 shows the details of Zn content, lattice constant, grain size and optical band gap of $Cd_{1-x}Zn_xS$ thin films.

Fig. 1 shows the XRD pattern of $Cd_{1-x}Zn_xS$ films for Zn content between x=0 and x=0.8. A comparison of the peak position (2θ values) of the JCPDS XRD spectra data suggests that the as-deposited films have both (zincblende) cubic and (wurtzite) hexagonal structure with the peaks corresponding to (111), (002), (103), (311), (100), (101), (200), (110), (220), (112). It was also observed that the lattice constant gradually decreases as Zn content (x value) increases (Table 1).

Table 1. A summary of lattice constant, grain size from XRD and optical bandgap for varying Zn content.

Zn content (x value)	Lattice constant Hex a Å	Lattice constant Hex c Å	Lattice constant Cubic a Å	Grain size (XRD) g nm	Band gap Eg (eV)
x = 0	4.1123	6.6516	5.8006	8.75	2.48
x = 0.2	4.0845	6.6342	5.7240	8.32	3.05
x = 0.4	3.9681	6.5208	5.6821	5.87	3.35
x = 0.66	3.7932	6.4030	5.4927	3.73	3.49
x = 0.8	3.7016	6.2911	5.4205	3.57	3.62

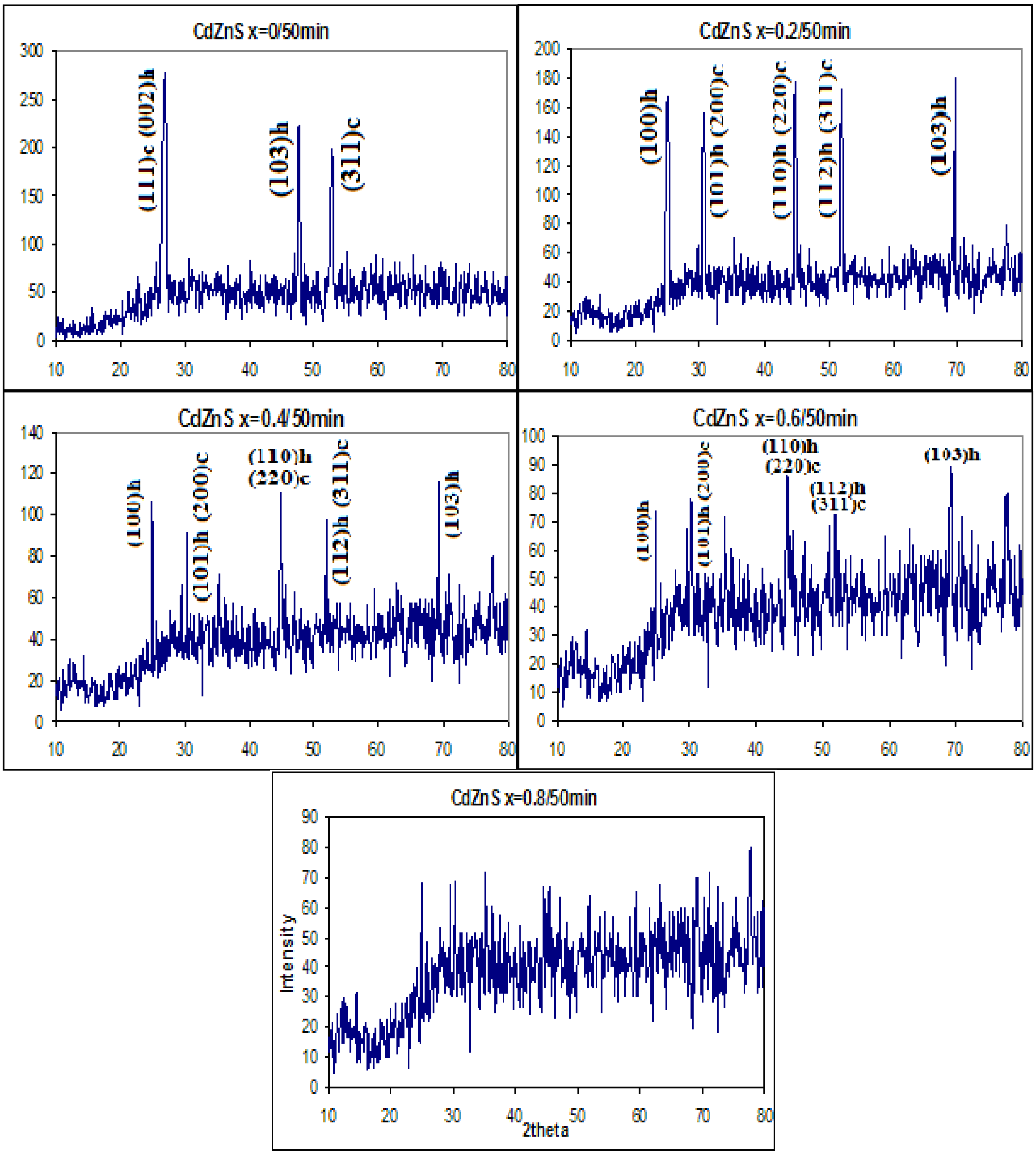


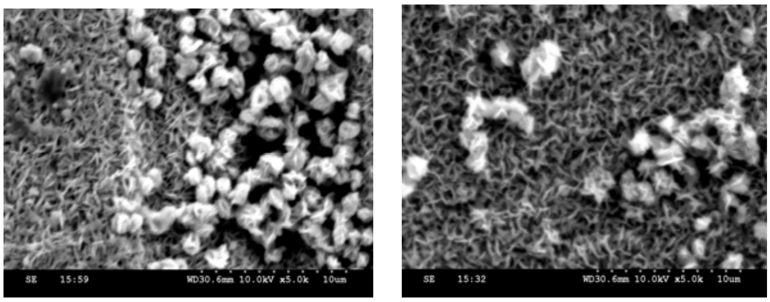
Fig. 1. XRD pattern of $Cd_{1-x}Zn_xS$ films for varying Zn content. (a) For x=0 (b) For x= 0.2 (c) For x= 0.4 (d) For x= 0.66 (e) For x= 0.8

The average grain size (g) has been obtained from the XRD patterns using Debye-Scherrer's formula, [6-8]

$$g = K\lambda / \beta \cos\theta$$

Where,
K = constant taken to be 0.94,
λ = wavelength of X-ray used (1.542Å),
β = FWHM of the peak and
θ = Bragg's angle.

The SEM micrograph shows smoother and more uniform films with fibre like structure as Zn content increases (Fig. 2). It is observed that the grain size decreases with increase in Zn content. The improved fibrous films may useful for gas sensing applications.



(a) x=0.2 *(b) x= 0.8*

Fig. 2. SEM of $Cd_{1-x}Zn_xS$ films (a) x=0.2 (b) x= 0.8

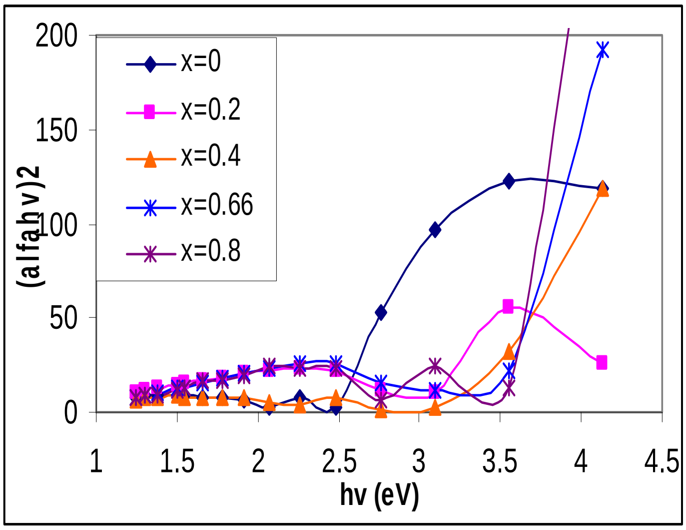


Fig. 3. Plot of $(\alpha h\nu)^2$ vs $h\nu$ for all CdZnS thin films.

The band gap Eg was determined from absorbance data by plotting $(\alpha h\nu)^2$ versus $h\nu$ and then extrapolating the straight line portion to the energy axis at $\alpha = 0$. The band gap energy Eg obtained for each Zn content is different. For higher Zn content (x=0.8) the band gap is 3.62eV and for lower Zn content (x=0) it is 2.48eV. The band gap of other films is intermediate (Fig. 3 and Table 1).

4. Conclusions

$Cd_{1-x}Zn_xS$ nano-crystalline thin films have been grown successfully by modified CBD technique. [6] The structural, morphological and optical energy bandgap characteristics have been studied. It is concluded that the method is useful for deposition of fibrous (nano-wires) $Cd_{1-x}Zn_xS$ thin films, also a step toward the development of cadmium free, low cost $Cd_{1-x}Zn_xS$ thin film solar cells. The wider bandgap of the deposited films makes them suitable for optoelectronic devices, for instance window layers in solar cells.

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