

Physical Properties of $Zn_xCd_{1-x}S$ Nanocrystalline Layers Synthesized by Solution Growth Method

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Abstract In recent years, zinc cadmium sulphide ($Zn_xCd_{1-x}S$) alloy compounds have paid much attention in the fields of opto-electronics, particularly in photovoltaic devices because of its tunable energy gap and the lattice parameters. The energy band gap of $Zn_xCd_{1-x}S$ is controlled by the change of Zn-composition in order to suit the material properties with that of absorber material in solar cells. In this paper, we report on the effect of Zn-composition on physical properties of $Zn_xCd_{1-x}S$ thin films deposited on corning glass substrates by solution growth method. The layers were prepared for different 'x' values that vary in the range, 0 – 1.0 at. %. The as-grown layers were characterized using EDAX, XRD, SEM, and UV-Vis-NIR spectrophotometers. All the layers showed a strong (002) plane as the preferred orientation that exhibited the hexagonal crystal structure. The composition of the layers agrees approximately with that of the elements in the solution. The films showed an average optical transmittance of 72 % at a zinc composition of 0.75 with a band gap of 3.88 eV.

Keywords $Zn_xCd_{1-x}S$ films, Solution growth, Composition, Structure, Optical properties

1. Introduction

In recent years, semiconductor materials have received renewed interest due to their novel properties. Among a variety of semiconductor materials, the wide-band gap binary II–VI compounds and their alloys have been investigated most extensively for their potential application in different fields such as opto-electronic devices[1], nonlinear optical and luminescence devices[2,3] because of the quantum-size effect[4,5], especially their tunable optical property [6,7]. Alloying of semiconductors is one of the simplest techniques used for tailoring the energy band gap, lattice parameter, electronic and optical properties[8]. Generally in alloys, the lattice parameter varies linearly with composition and follows the Vegard's law. In some of the II–VI alloy materials, the energy gap variation with composition is not very smooth and they show slight bowing. In a wider region however, the band gap tailoring also obeys Vegard's law[9]. Currently, the ternary II–VI semiconductor materials have attracted more interest than the binary II–VI compounds due to their better physical properties compared to other materials, especially their tunable optical properties which could be controlled by their constituent mole-fraction, particle size, and morphology. Among the different ternary II–VI semiconductors, $Zn_xCd_{1-x}S$ has been widely used as a wide band

gap material in heterojunction solar cells[10–12] and in photoconductive devices[13]. Moreover, in $CuGaSe_2$ heterojunction solar cells, the use of $Zn_xCd_{1-x}S$ led to an increase of photocurrent by minimising the electron affinity mismatch between the two semiconductors. Further, $Zn_xCd_{1-x}S$ can also be used as a window material in the fabrication of $p-n$ junction solar cells without lattice mismatch in the devices based on quaternary materials like $CuIn_xGa_{1-x}Se_2$ or $CuIn(S_zSe_{1-z})_2$ [14]. Although $Zn_xCd_{1-x}S$ layers have been synthesized by different techniques[10–14], solution growth method is a simple technique to grow thin films that are uniform and free from pinholes. This method is also known as chemical bath deposition and normally performed under the atmospheric pressure at ambient temperatures. In this paper, we report on the effect of alloying on the physical properties of $Zn_xCd_{1-x}S$ thin films deposited on corning glass substrates by solution growth method.

2. Experimental Details

Thin films of $Zn_xCd_{1-x}S$ were prepared by simple and economic process, chemical bath deposition method for different Zn-composition that varied in the range, 0 – 1.0 at. %. The deposition bath contained 0.1M aqueous solutions of zinc acetate, cadmium acetate and thiourea, taken as precursors for Zn, Cd and S respectively. The mixture was stirred well using a controllable magnetic stirrer. Ultrasonically cleaned Corning 7059 glass substrates were vertically dipped in the deposition bath while stirring of the solution continues. The deposition was carried out at a bath tem-

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perature of 70°C for a reaction time of 30 min. A thin layer with bright yellow color was formed on the surface of the substrates. These substrates were removed from the beaker washed with de-ionized water to remove the loosely adherent powder precipitates in the solution during deposition and then dried in hot air. The as-grown layers were characterized by studying the structural, optical and electrical properties. The crystallinity of the films was measured using a Siefert X-ray diffractometer with Cu-K α radiation source ($\lambda=1.54$ Å). The morphological properties of the films were evaluated using the Hitachi scanning electron microscope (SEM). The optical transmittance measurements were performed using a Hitachi UV-Vis-NIR spectrophotometer.

3. Results and Discussion

Pure CdS films appeared bright yellow in color and became pale yellow as more Zn replaces Cd in the layers. All the layer were uniform and strongly adherent to the substrate surface.

3.1. Film Composition

Fig.1. shows the chemical composition of $ZnCdS$ films evaluated using EDAX. The EDAX spectra indicated well defined peaks corresponding to Zn, Cd and S in addition to O. All the grown films showed Se deficiency irrespective of the Zn-composition. The presence of oxygen in the layers was due to the surface contamination because the films were prepared using a non vacuum technique, CBD and/or also due to the incomplete reaction of the bath mixtures.

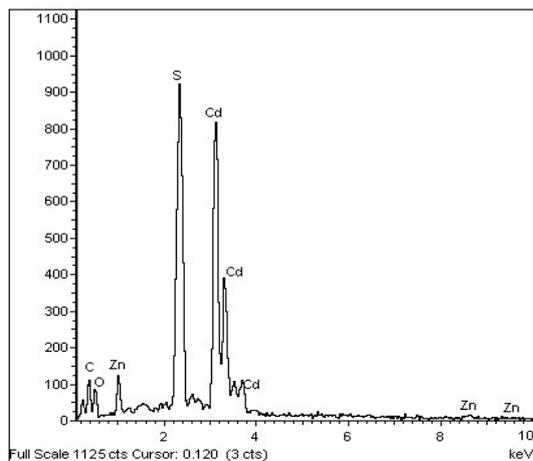


Figure 1. EDAX spectrum of $Zn_{0.25}Cd_{0.75}S$ film

3.2. Structural Properties

The crystallographic studies made using X-ray diffraction analysis clearly indicated the effect of alloying on the crystalline quality of the grown layers. The X-ray diffraction spectra of $Zn_xCd_{1-x}S$ films with three different 'Zn' composition, $x = 0.25, 0.5$ and 0.75 are shown in Fig. 2. The X-ray diffraction patterns of the layers showed the same preferential orientation without secondary phases in the investigated composition range. The X-ray diffraction patterns mainly

exhibited peaks related the (002), (101), (110) and (112) reflections of the hexagonal structure. All the layers exhibited the (002) crystal plane as the preferential orientation and its intensity increases with the increase of zinc content in the layers. As the samples are originated from hexagonal structure, no phase transition occurred with the increase of Zn/Cd ratio in the films. The position of diffraction peaks shifted to higher 2θ values with the increase of Zn-content. The X-ray diffraction results are in good agreement with the reported results[15,16].

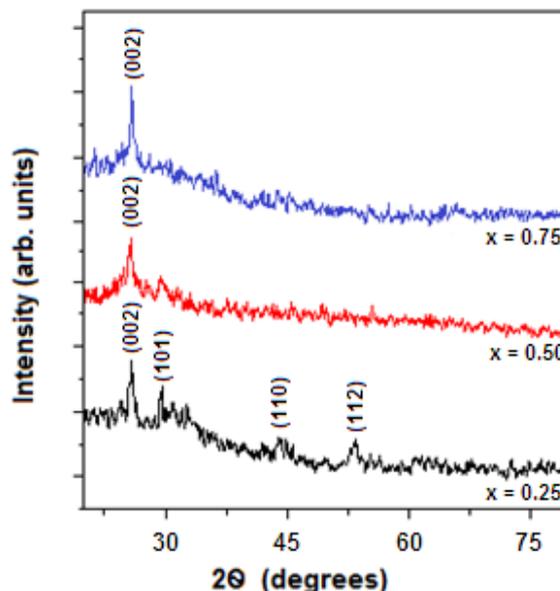


Figure 2. X-ray diffraction profiles of $Zn_xCd_{1-x}S$ films

This shift in the diffraction angle is expected since there is no phase separation or separated nucleation of ZnS or CdS in the $Zn_xCd_{1-x}S$ phase and/ or due to the changes occurred in the lattice parameters with the increase of Zn-content. The values of a and c for films prepared at $x = 0$, pure CdS are 4.25 Å and 6.73 Å, respectively. These values are in good agreement with the reported data for hexagonal CdS films [17]. Although the lattice constants, a and c decreased linearly with the increasing of 'Zn' concentration, the observed variation in a is marginal compared to that of c . This decrease in the value of 'c' is due to the Zn^{2+} incorporated in the CdS lattice entering into lattice and/or interstitial sites because of the smaller radius of Zn^{2+} ion (0.74Å) compared with that of Cd^{2+} (0.97 Å). The crystallite size (D) of $Zn_xCd_{1-x}S$ films prepared with different Zn compositions, x were calculated using the Scherrer's formula[18]. The evaluated grain size of the layers with the Zn-composition, x varied from 45 nm to 72 nm.

Fig.3 shows the SEM images of the films synthesized at different zinc compositions. The surface morphology of $Zn_xCd_{1-x}S$ films is found to be similar to that of CdS. The grains on the film surface were more compact and have dense structure. Also, the surface of the layer is covered with equal sized grains that are unevenly distributed. This may be probably due to the colloidal particles formed in solution. Further, the size of the particle increased with the increase of

Zn-content. The estimated particle size of the deposited films by SEM analysis is in the range, 40 – 70 nm.

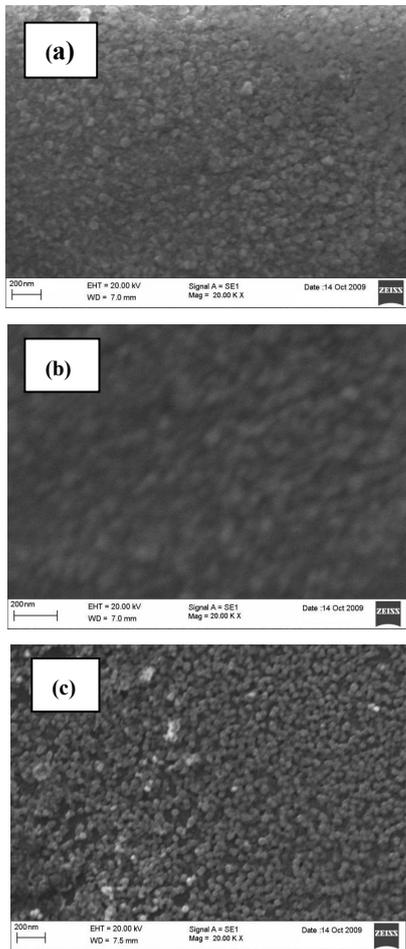


Figure 3. SEM micrographs of $Zn_xCd_{1-x}S$ films; (a) $x=0.25$, (b) $x=0.5$ and (c) $x=0.75$

Fig. 4 indicates the influence of alloying on the optical transmittance, T versus wavelength, λ characteristics of $Zn_xCd_{1-x}S$ films measured in the wavelength range, 300-1800 nm. The transmittance of the films increased from 74% to 85% above the fundamental absorption edge with increase of Zn-content. It could be observed from Fig. 4 that $Zn_xCd_{1-x}S$ films had a transparency in the visible region, which indicates better crystallinity in the films. Also, the fundamental absorption edge of the films shifted towards the shorter wavelength side with the increase of Zn-composition. The optical studies revealed that the absorption coefficient, α increased with the increase of composition upto 0.75. This shift in the α might be due to the increase of band gap as a function of composition ($x \leq 0.75$). The energy band gap was determined from the $(\alpha h\nu)^2$ versus $h\nu$ plots where the interception of linear portion onto the energy axis gives the energy band gap of the material. The variation of band gap of $Zn_xCd_{1-x}S$ films with 'Zn' composition was found to be linear, which is due to the fact that the band gap of ZnS is greater than that of CdS[9]. The optical band gap of the films varied in the range, 3.4 - 3.9 eV when the composition varied from 0.0 to 1.0. This shift in the energy band gap towards

higher energy side is consistent with the behavior reported in literature[19,20]. $Zn_{0.75}Cd_{0.25}S$ films showed a band gap of 3.88 eV, which is shown in inset of Fig.4. This continuous change in band gap with increasing proportion of zinc again confirms the formation of a solid solution. The larger energy band gap determined for the films grown at higher Zn values might be attributed to the incorporation of hydroxyl groups in the films and /or due to the presence of secondary phases in small quantity that were not observed in the XRD pattern.

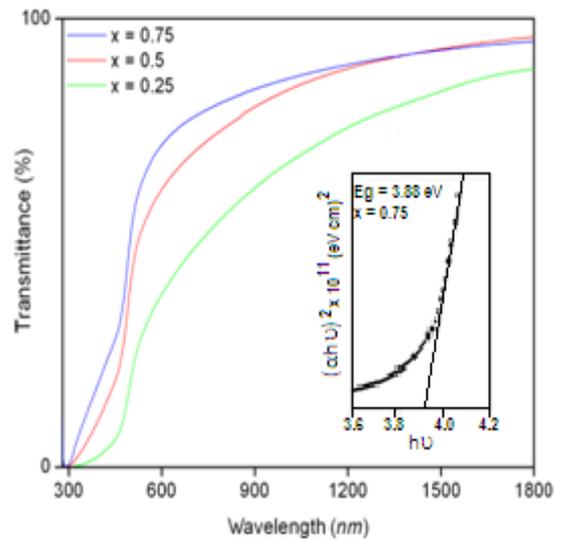


Figure 4. Transmittance versus wavelength plot of $Zn_xCd_{1-x}S$ films (inset shows $(\alpha h\nu)^2$ versus $h\nu$ plot for $Zn_{0.75}Cd_{0.25}S$ film)

5. Conclusions

Thin films of $Zn_xCd_{1-x}S$ have been successfully prepared by simple and economic process, chemical bath method with different 'Zn' compositions that varied in the range, 0 – 1 % at a constant bath temperature of 70°C for a reaction time of 30 min. All the layers showed a strong (002) plane as the preferred orientation that exhibited the hexagonal crystal structure. The variation of lattice constants with Zn- composition showed linear behavior. The evaluated average grain size was found to vary from 45 nm to 76 nm. SEM micrographs revealed the grains on the film surface were more compact and have dense structure. The films showed an average optical transmittance of 72 % at a zinc composition of 0.75 and exhibited a band gap of 3.88 eV. By suitably controlling the Zn-composition in the layers, the $Zn_xCd_{1-x}S$ films may have minimum lattice mismatch that that of pure CdS with some of the absorber layers, particularly with chalcopyrite compounds.

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