

Some Properties of $Zn_xCd_{(1-x)}S$ and $Zn_xCd_{(1-x)}S(In)$ Thin Films Prepared by Pyrolytic Spray Technique

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Abstract: The structural, electronic and optical properties of $Zn_xCd_{(1-x)}S$ and $Zn_xCd_{(1-x)}S(In)$ thin films ($0.0 \leq x \leq 0.6$) fabricated using the chemical spraying method have been investigated. The films are deposited on glass substrates at 420 °C substrate temperature. The related optical data are recorded in the wavelength range 200-700 nm. In addition, the absorption coefficient is determined and correlated with the photon energy in order to estimate the direct transition energy bandgap. Our X-ray diffraction investigations confirm the preferential orientation of these polycrystalline films along the hexagonal (002), (100) and (101) planes. Also, film surface structure is studied using an optical microscope. Thin films of $Zn_xCd_{(1-x)}S$ are known to have properties in between those of CdS and ZnS. Because of the addition of ZnS, the $Zn_xCd_{(1-x)}S$ band structure has a larger energy gap than CdS. This makes the material much more attractive for the fabrication of solar cells. Indeed, the best CdS solar cells have been prepared on $Zn_xCd_{(1-x)}S$ substrates.

Keywords: Thin Film, Spray Pyrolysis, ZnCdS

Introduction

There has earlier been an increasing interest (Mathew *et al* 1995, and Kwok and Siu 1979) in the electronic and optical properties of the chemically sprayed CdS thin films. One reason for this is that the chemical spraying method is still regarded as one of the simplest and most economical methods of preparing polycrystalline films of reasonably good quality. Although much work has been done on the electronic and optical properties of polycrystalline CdS films, less information, is available on the ternary $Zn_xCd_{(1-x)}S$ system. Thin films of $Zn_xCd_{(1-x)}S$ are known (Dachraoui and Vedel 1989) to have properties in between those of CdS and ZnS. Because of the addition of ZnS, the $Zn_xCd_{(1-x)}S$ band structure has a larger energy gap than CdS. This makes the material much more attractive for the fabrication of solar cells.

$Zn_xCd_{(1-x)}S$ thin films have been widely used as a wide bandgap window material in heterojunction photovoltaic solar cells (Shaiw *et al* 1978, Dachraoui and Vedel 1985, Reddy *et al* 1992, Yamaguchi *et al* 1999, Olea and Sebastian 1998, and Uppal *et al* 1983) and in photoconductive devices (Torres and Gordillo 1997). In solar cell systems, where CdS thin films have been proved to be useful, partial substitution of Zn for Cd increases the optical window of the heterojunction and also the diffusion potential (Oladeji *et al* 2000, Kulkarni *et al* 2001 and Valkonen *et al* 1998). Moreover, in heterojunction solar cells using $CuGaSe_2$, the use of $Zn_xCd_{(1-x)}S$ instead of CdS can lead to an increase in photocurrent by providing a match in the electron affinities of the two materials. This hexagonal $Zn_xCd_{(1-x)}S$ ternary compound is also potentially useful as a window material for the fabrication of p-n junctions without lattice mismatch in the devices based on quaternary materials like $CuGaSe_2$ (Reddy *et al* 1992) or $CdSe_{1-y}S_y$ (Torres and Gordillo 1997). $Zn_xCd_{(1-x)}S$ thin films have been prepared by a variety of techniques, which include spray pyrolysis (Kwok and Chau 1980, and Oztas and Bedir 2001), sintered (Kumar *et al* 1998, and Sebastian and Narvaez 1996), molecular beam epitaxial growth

(Telfer *et al* 2000), and screen printing method (Sebastian and Ocampo 1995). Initial studies (Mathew *et al* 1995, and Kwok and Siu 1979) have demonstrated that the chemically sprayed films have high carrier densities and resistivities. Both the energy gap and the film composition depend on the spraying solution composition (Chu and Chu 1995). n-ZnCdS / p-CdTe polycrystalline thin film solar cells have been fabricated by laser evaporating CdTe onto sprayed ZnCdS films. These study (Hussain *et al* 1991) has demonstrated that the cell has been a maximum efficiency of 7.6% for a cell area of 1 cm².

In this article the structural electronic and optical properties of $Zn_xCd_{(1-x)}S$ and $Zn_xCd_{(1-x)}S(In)$ thin films prepared using the chemical spraying method are investigated by varying the concentrations of cadmium and zinc and also by keeping Indium (0.25% In) fixed. Our main interest is the study of the transport properties, namely the resistivity, carrier density and the mobility changes as a function of composition in the dark. The absorption coefficient (α) is determined and correlated with the photon energy in order to estimate the direct bandgap energy of the films.

Experimental Procedure

Film preparation: The $Zn_xCd_{(1-x)}S$ and $Zn_xCd_{(1-x)}S(In)$ thin films were prepared using spray pyrolysis technique (Oztas and Bedir 2001). $ZnCl_2$ and $CdCl_2$ were used to supply Zn and Cd, respectively while thiourea $(NH_2)_2CS_2$ was used to provide sulfur. Indium dopant was added in the form of $InCl_3$. All films were deposited at 420°C substrate temperature and a spray rate of about 3 ml / min. The film thickness was determined by weighing each sample before and after each deposition and using a CdS bulk density of 4.32 gm/cm³. Film thickness varied in the range 1.1 to 3.2 μm . No correlation was observed between the film thickness and the zinc concentration.

Measurements: In this study the Van der Pauw technique (Mzard *et al* 1990) is used to evaluate the

carrier density and the mobility at room temperature in the dark. Evaporated Indium contacts were used for the measurement. The crystallinity of the films were determined using a Phillips X-ray powder diffractometer with monochromated high intensity $CuK \alpha_1$ radiation ($\lambda=1.5405\text{\AA}$). Diffraction spectra of all films were taken over the range of $20^\circ \leq 2\theta \leq 50^\circ$. The optical absorption characteristics of the $Zn_xCd_{(1-x)}S$ and $Zn_xCd_{(1-x)}S(In)$ thin films were measured with a Jasco 7800 Model UV-Visible double beam spectrometer in the range of 300-700 nm. The optical absorption coefficient (α) was calculated from the relation:

$$\alpha = -\frac{1}{t} \ln\left(\frac{T}{1-R}\right)$$

where T is the transmittance, R the reflection, and t the thickness of the films. The optical energy bandgap (E_g) of the films is evaluated from the absorption coefficient by fitting the data to

$$(\alpha h\nu) = B(h\nu - E_g)^{1/2}$$

where B is a constant which contains the optical matrix element and $h\nu$ the photon energy. The variation in energy band gap with respect to the compositional parameter x is discussed in the following section.

Results

We have found that the carrier density of the deposited $Zn_xCd_{(1-x)}S$ films vary from 15×10^{16} to $39 \times 10^{16} \text{ cm}^{-3}$ whereas In-doped $Zn_xCd_{(1-x)}S$ films vary from 48×10^{16} to $67 \times 10^{16} \text{ cm}^{-3}$ as composition x increases from 0.0 to 0.6. The variation of mobility and carrier density with x in $Zn_xCd_{(1-x)}S$ and $Zn_xCd_{(1-x)}S(In)$ thin films is shown in Fig. 1(a) and 1(b). It was also observed that the carrier densities were quite high, of the order of 10^{16} cm^{-3} and increased somewhat with an increase in Zn concentration. The observed mobilities were low and decreased rapidly with increasing Zn concentration, as shown in Fig. 1(a).

Fig. 1(b) show the carrier density and mobility for $Zn_xCd_{(1-x)}S(In)$ thin films with different values of composition x. It was observed that while the carrier density increased with the addition of zinc, the mobility decreased with increasing zinc concentration. It is obvious from the Fig's 1(a) and 1(b) that the indium doped films show lower resistivity with higher mobility and carrier density than those of undoped films, due to the incorporation of indium.

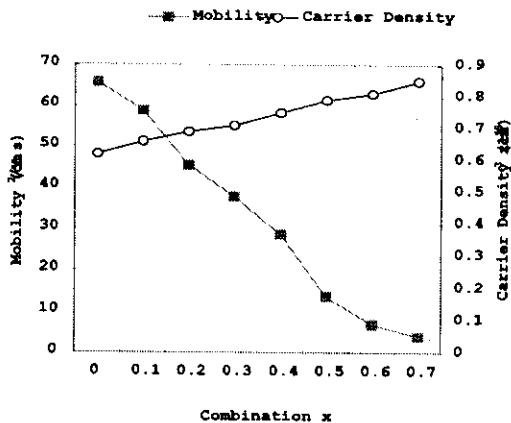


Fig. 1(b): Mobilities and carrier densities for different combination x in $Zn_xCd_{1-x}S(In)$ thin films

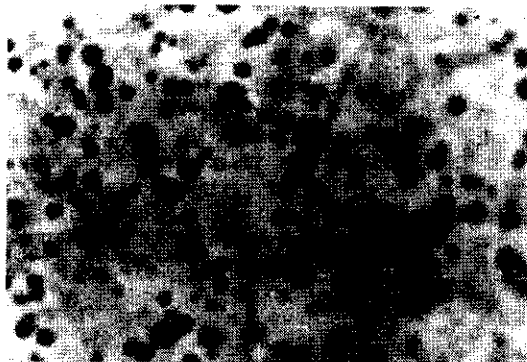


Fig. 2(a): Optical micrograph (250x) of CdS thin film

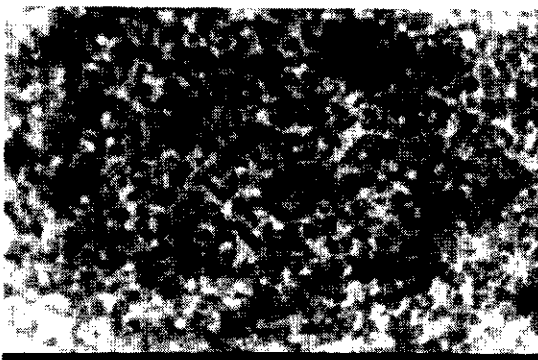


Fig. 2(b): Optical micrograph (250x) of $Zn_{0.1}Cd_{0.9}S$ thin film

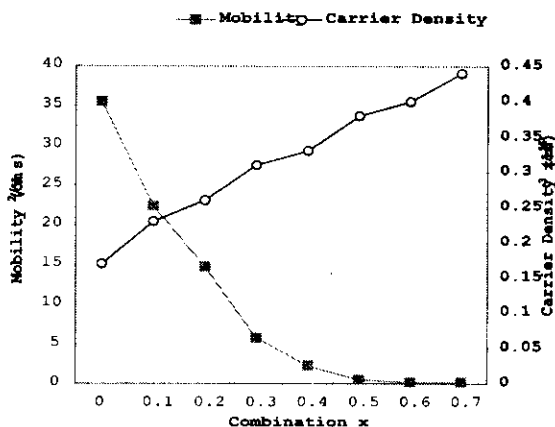


Fig. 1(a): Mobilities and carrier densities for different combination x in $Zn_xCd_{1-x}S$ thin films

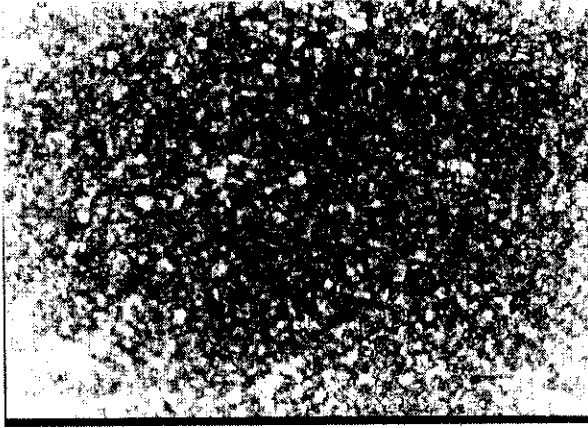


Fig. 2(c): Optical micrograph (250x) of $Zn_{0.3}Cd_{0.7}S$ thin film

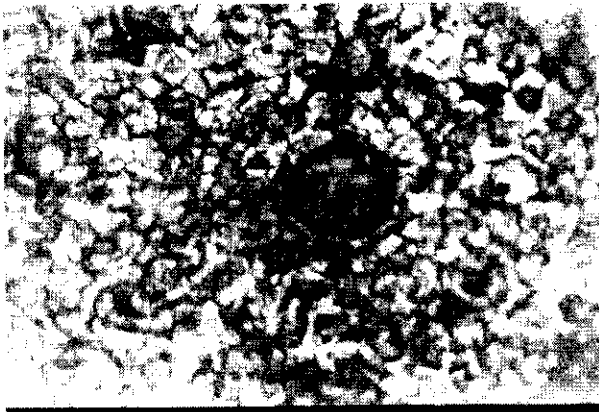


Fig. 2(d): Optical micrograph (250x) of $Zn_{0.4}Cd_{0.6}S$ thin film

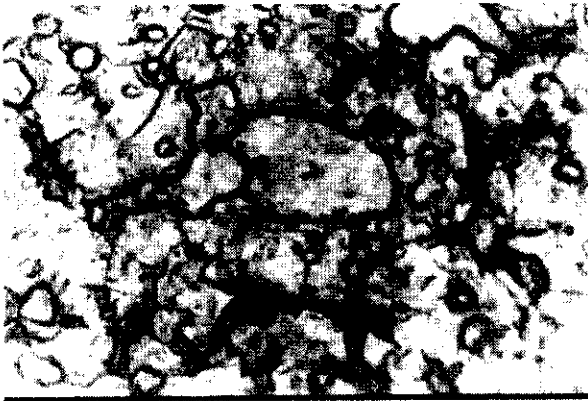


Fig. 2(e): Optical micrograph (250x) of $Zn_{0.4}Cd_{0.6}S(In)$ thin film

Variations in surface morphology with composition were observed using optical microscopy. Fig. 2 shows optical micrographs (250x) of typical $Zn_xCd_{(1-x)}S$ and $Zn_xCd_{(1-x)}S(In)$ films with different ratios of cadmium to zinc. In general, the film surface becomes increasingly coarse as the zinc concentration increases. The inclusion

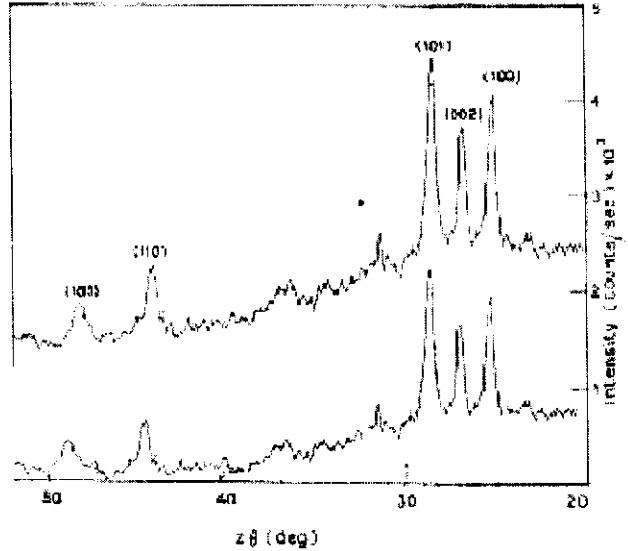


Fig. 3: X-ray diffraction pattern of $Zn_{0.5}Cd_{0.5}S$ (below) and $Zn_{0.5}Cd_{0.5}S(In)$ (above) thin films on glass substrate at 420 °C

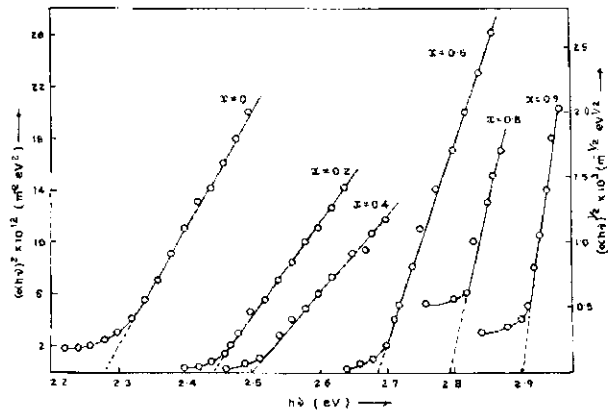


Fig. 4: The plots of $(\alpha hn)^2$ (for $0.0 \leq x \leq 0.6$) and $(\alpha hn)^{1/2}$ (for $x > 0.6$) against hn of $Zn_xCd_{1-x}S$ thin films

of indium as a dopant appears to increase grain size. Grain size and surface roughness also vary as a function of film thickness. Thicker films (greater than 2 μm thick) have rough and undulating surfaces with grain size of 1-4 μm . Thinner films (less than 2 μm thick) have smoother surfaces, less defined grain boundaries, and grain sizes less than 1 μm . In general, the addition of zinc to sprayed $Zn_xCd_{(1-x)}S$ and $Zn_xCd_{(1-x)}S(In)$ films results in structurally inferior films as evidenced by gross film non-uniformities. Consequently, it may be necessary to limit the degree of zinc present in these films for applications like solar cells, particularly when spray pyrolysis is used as the fabrication technique.

Fig. 3 shows the x-ray spectrum for $Zn_xCd_{(1-x)}S$ and $Zn_xCd_{(1-x)}S(In)$ films deposited at the same substrate temperature. Comparison of this data to randomly oriented powder diffraction data confirms a hexagonal (101) orientation. Though hexagonal peaks are clearly visible in Fig. 3, the convolution of these peaks with the corresponding cubic phase peaks does not rule out the

possibility that these films contain both cubic and hexagonal phases. Diffraction peaks corresponding to In-doped films were sharper and narrower possibly due to the larger grains present in these films with the prominent X-ray diffraction peaks corresponding to (100), (002), (101), (110), and (103) planes.

The optical energy gap of the $Zn_xCd_{(1-x)}S$ thin films was estimated by the optical absorption measurements of the films as a function of wavelength in the range 2.2 eV to 3.5 eV from which absorption co-efficient (α) was obtained. Plots of $(\alpha hv)^2$ and $(\alpha hv)^{1/2}$ against hv were made Fig. 4. $(\alpha hv)^2$ vs. hv plots yielded straight line over the range $0 \leq x \leq 0.6$. In contrast, for $x > 0.6$ straight lines were obtained when $(\alpha hv)^{1/2}$ was plotted against hv . This is indicative of the fact that the films are crystalline for $0 \leq x \leq 0.6$ and amorphous beyond this range. By this technique, we observed an increase in bandgap with the Zn concentration and In-doping films did not appear to affect the optical bandgap.

Discussion

We have made a through study of the effects of adding zinc to chemically sprayed CdS thin films. Deposited films were single phase in nature as shown by Vegard-like variations in lattice size and optical bandgap with film composition. Unlike CdS thin films, $Zn_xCd_{(1-x)}S$ thin films were visibly inferior as evidenced by increased roughness and the presence of gross microstructural non-uniformities.

The electrical and optical properties of Zn-containing films were similar to those of CdS thin films except that the mobility was much lower. In fact, the mobility decreased to very low values when the zinc concentration became comparable to that of cadmium. It was observed in this study that zinc lowered the film mobility while increasing the carrier density slightly. Indium doped films exhibited higher mobilities and carrier densities and the same decrease in mobility with increasing Zn concentration. Chemisorbed oxygen is known to affect the transport properties of II-IV compound films primarily through either serving as a compensating acceptor (in n-type films) or as an electron trap at grain boundaries. From our results, higher Zn concentrations appear to accentuate the detrimental effects of chemisorbed oxygen. One possibility is that the grain size of our films may be decreasing with increasing Zn concentration. The corresponding increase in grain boundary surface area (and increased chemisorbed oxygen) in addition to the smaller grains may be responsible for the observed in film mobility with increasing Zn.

Conclusion

We have investigated the structural, electronic and optical properties of chemically sprayed $Zn_xCd_{(1-x)}S$ and $Zn_xCd_{(1-x)}S(In)$ thin films ($0.0 \leq x \leq 0.6$) onto glass substrates. We have observed that, while reasonably good solid solutions of $Zn_xCd_{(1-x)}S$ can be produced by adjusting the spraying ingredients, the resulting film structure deteriorates with increasing zinc concentration. The addition of zinc also reduces the film mobility significantly. Film structure increases somewhat the addition of indium as a dopant. These latter films show higher mobilities and carrier densities with a corresponding decrease in film resistivity. Grain size was also observed to increase with In-doping. Surface morphology study as well as X-ray diffraction data shows that good crystallinity is obtained up to a zinc fraction of 0.4. For $x > 0.6$ the films appear to develop an amorphous character.

If these films are to be used in the fabrication of solar cells, our results suggest that a zinc concentration of no more than 10% should be used and may be a heterostructure such that zinc can be added mainly in

regions near the cell junction.

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