Effect of the Zn Concentration on the Characteristic Parameters of $Zn_xCd_{1-x}S$ Thin Films Developed by Spraying Pyrolysis Method Under the Nitrogen Atmosphere

Metin BEDİR, Refik KAYALI and Mustafa ÖZTAŞ
Department of Physics Engineering, University of Gaziantep,
27310, Gaziantep-TURKEY
bedir@gantep.edu.tr

Abstract

The electronic and optical properties of $Zn_xCd_{(1-x)}S$ thin films ($0.0 \leq x \leq 0.7$) fabricated using the chemical spray method have been investigated in nitrogen atmosphere. 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. The crystallite size and degree of preferential orientation were found to decrease with the increase of x and to improve upon annealing in vacuum at $\cong 600°C$. The transmission edge shifted towards shorter wavelengths with increase of x in agreement with the expected shift in energy band gap. The films were found to exhibit room temperature resistivity variation in the range 100-1000 Ωcm with composition.

Key Words: Spray Pyrolysis, Thin Film, ZnCdS

1. Introduction

There has been increasing interest [1] in the electronic and optical properties of the chemically sprayed CdS thin films. One reason for this is that the chemical spray 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 [2,3] 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 [4-9] and in photoconductive devices [10]. 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 [11,12]. 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 devices based on quaternary materials like $CuIn_xGa_{1-x}Se_2$ [13] or $CuIn(S_xSe_{1-x})_2$[14]. $Zn_xCd_{1-x}S$ thin films have been prepared by a variety of techniques, including spray pyrolysis [11,15], ion beam deposition [16], molecular

beam epitaxial growth [17,18], and screen printing method [19,20]. Initial studies [2,3] 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 [21]. These relationships deviate somewhat from exact linearity. Very little information, however, has been given on the carrier density and the mobility. The evaporated films have been reported to have much higher conductivities [22].

In this article, the electronic and optical properties of $Zn_xCd_{(1-x)}S$ thin films prepared using the chemical spraying method are investigated by varying the concentrations of zinc in the range

$(0.0 \leq x \leq 0.7)$. Our main interest is the study of the transport properties, namely the resistivity, carrier density and the mobility changes in the dark as a function of composition. The absorption coefficient α is determined and correlated with the photon energy in order to estimate the direct bandgap energy of the films.

2. Experimental Details

$Zn_xCd_{1-x}S$ thin films were prepared using the chemical spray method [11,15]. The apparatus used for the development of the thin films based on the spraying pyrolysis technique has been desingned and developed in our laboratory. The schematic diagram of this apparatus is shown in Figure 1. The spray apparatus was enclosed in a chamber in order to keep the process in a controlled atmosphere and feedback circuits were used to control the substrate temperature under changing spray conditions. The substrate temperature was measured using a chromel-allumel thermocouple placed in good thermal contact with the substrate surface. The substrate temperature has a great influence on the deposition process. In the process, the spray rate, the size of the sprayed particles and the spray pattern are strongly influenced by the geometry of the spray nozzle used [27].
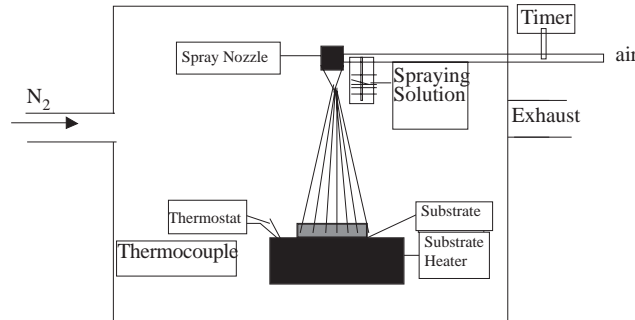

Figure 1. Schematic diagram of the spray pyrolysis system.

In this technique, a mist of a spray solution was driven to the surface of a heated substrate where a pyrolytic reaction takes place, leaving a solid film plus some volatile compounds. $ZnCI_2$ and $CdCI_2$ were used to supply Zn and Cd, respectively while thiourea $(NH_2)_2CS$, was used to provide sulphur for the $Zn_xCd_{1-x}S$ thin films. $Zn_xCd_{1-x}S$ thin films were deposited at $420°C$ substrate temperature. All films were annealed at about $600°C$ for 30 min in $2x10^{-5}$ torr vacuum to decrease the resistivity of the alloy films by removal of acceptor-like oxygen levels. The film thickness was determined by weighing each sample before and after each deposition. Thickness of $Zn_xCd_{1-x}S$ thin films was in the range of 1.0-1.2 μm. No correlation was observed between the film thickness and the zinc concentration. All samples were subsequently etched in a dilute mixture of hyrochloric acid (HCl) to remove rough surfaces and reduce the influence of surface effects. Ohmic contacts were then obtained by the vacuum evaporation of high purity indium onto the films. The Van der Pauw method was used to measure the electrical properties of the films.

3. Results and Discussion

In this study the Van der Pauw technique [23] is used to evaluate the film resistivity, the carrier density and the mobility at room temperature in the dark. Evaporated Indium contacts were used for the measurements.

The optical absorption characteristics of the $Zn_xCd_{(1-x)}S$ thin films were measured with a Jasco 7800 Model UV-Visible double beam spectrometer in the range of 300-700 nm. The measurement values the crystallite size d, energy gap E_g and resistivity ρ of sprayed $Zn_xCd_{1-x}S$ thin films are shown in Table 1.

Table 1. Crystallite size d, energy gap E_g and resistivity ρ of sprayed $Zn_xCd_{1-x}S$ thin films.

Composition x	Crystallite size d[A]	Energy gap E_g[eV]	Resistivity ρ [Ωcm]
0.00	455	2.40	100
0.20	395	2.66	215
0.40	330	2.72	715
0.60	265	3.15	953
0.70	195	3.30	1155

We have found that the resistivity of the deposited $Zn_xCd_{(1-x)}S$ thin films increase from $\sim$100 to more than 10^3 Ωcm as composition x increases from 0.0 to 0.7, as shown in Figure 2. The long wavelength transmission of the films was observed to fall 70-80%, high enough for solar cell applications. However, for such applications the electrical resisitvity of the present undoped films (Table 1) is relatively high. A value of $\rho \geq 10^2$ ohm is known to produce significant resistive losses in the solar conversion efficiency. The resisitvity can be reduced through proper doping with shallow donor impurities (e.g. In) and/or post-preparation annealing. 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 concentation, as shown in Figure 3. From our results, it is shown that when the inter-grain barrier heights decrease, the resistivity of the thin film decreases while mobility of the thin film increases.
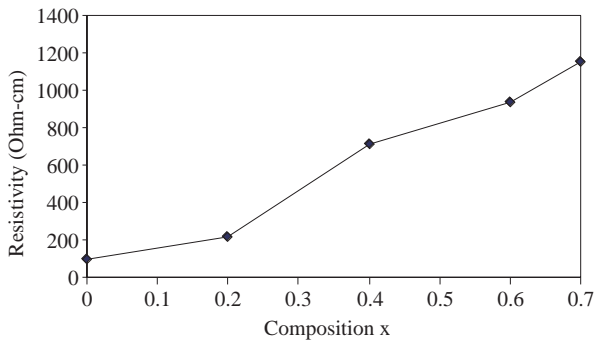

Figure 2. Change of resistivity in $Zn_xCd_{1-x}S$ thin films with composition x.
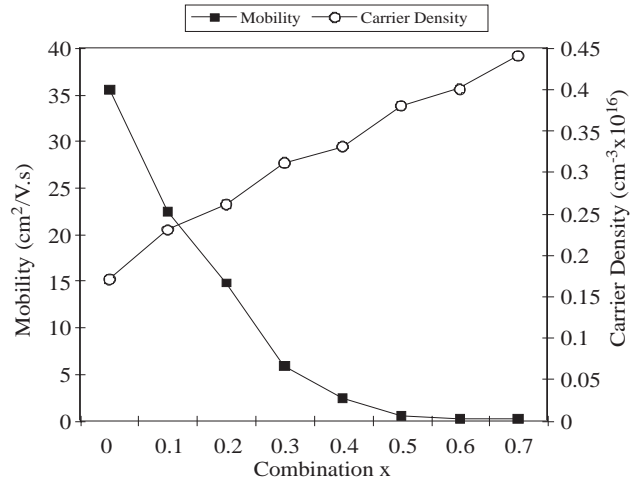
Figure 3. Mobilities and carrier densities for different combination x in $Zn_xCd_{1-x}S$ thin films.

Figure 4 shows the room temperature transmission spectra for the studied compositions ($0.0 \leq x \leq 0.7$). When the transmission is corrected for the reflection loss, it can attain a value of almost 100% for energies lower than the energy gap. The transmission edge shifts towards shorter wavelength with increasing x following the expected increase in the energy gap E_g. The values of E_g calculated from the threshold wavelength λ according to the relation

$$E_g = hc/\lambda \tag{1}$$

123

are given in Table 1. In Figure 5, we report the variation of the energy gap of the $Zn_xCd_{(1-x)}S$ thin films as a function of the Zn concentration. It was observed that the enegy gap of $Zn_xCd_{(1-x)}S$ thin films increased with the increasing composition x. This means that the resistivity of the films increased while the mobility of the films decreasing with the increasing the energy gap value of the films.
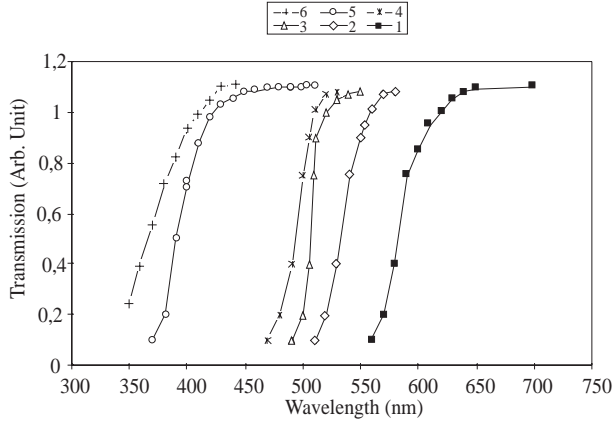

Figure 4. Transmission spectra of some $Zn_xCd_{1-x}S$ thin films. Curves 1, 2, 3, 4, 5, 6 were obtained for a Zn concentration of 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 respectively.
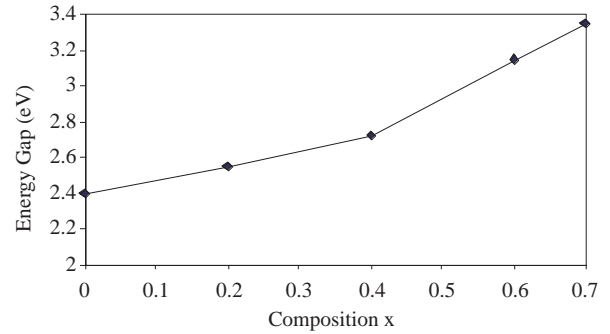
Figure 5. Change of energy band gap with zinc composition x in $Zn_xCd_{1-x}S$ thin films.

The crystallite size was estimated using the approximate formula

$$d = \lambda/D \cos\theta, \tag{2}$$

where λ is the wavelength, D is the angular line width at half maximum intensity and θ is the Bragg angle. The calculated values of d are given in Table 1. d is shown to decrease with increasing ZnS content.

We have studied the effects of adding zinc to chemically sprayed CdS thin films. Deposited films were single phase in nature as shown by Vegard-like [28] 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 ($0.15 \text{ cm}^2/\text{Vsec}$) when the zinc concentration became comparable to that of cadmium. This observation seems to contradict previous reports [25,26] that the mobility is relatively independent of the zinc concentration. It was observed in this study that zinc lowered the film mobility while slightly increasing the carrier density. 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, in addition to the smaller grains, may be responsible for the observation decreased of film mobility with increasing Zn. It was also seen the grain size of the films was decreased with the increasing zinc concentrations. Thus, the resistivity of the thin films decreases with the increasing grain size and also observed low mobility with the additional zinc concentrations.

4. Conclusion

We have investigated the structural, electronic and optical properties of chemically sprayed $Zn_xCd_{(1-x)}S$ thin films ($0.0 \leq x \leq 0.7$) onto glass substrates. We have observed that, while reasonably good solid solutions of $Zn_xCd_{(1-x)}S$ can be produced by adjusting the spray ingredients, the resulting film structure deteriorates with increasing zinc concentration. The addition of zinc to CdS increased the carrier densities but reduced the film mobility significantly. These latter films show higher mobilities with a corresponding decrease in film resistivity. The film crystallite size and degree of preferential orientation were found to decrease with the increase of x. The long wavelength optical transmission was found to be high enough for the utilization

of these films in solar cel applicaitons. However, for these applications the electrical resistivity of the present films should be reduced further through proper doping and/or post-preparation annealing. 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.

Acknowledgements

References

[1] W.C. Siu and H.L. Kwok, *J. Phys. D.,* **11,** 669, (1978).

[2] R.S. Feigelson, A. N'Diage, S.Y. Yin and R.H. Bube, *J. Appl. Phys.,* **48,** 3162, (1977).

[3] A. Banerjee, P. Nath, V.D. Vankar and K.L. Chopra, *Phys. Stat. Sol.* **(a), 46,** 723(1978).

[4] K.T.R. Reddy and P.J. Reddy, *J. Phys.* **D: 25**, 1345, (1992).

[5] B.M. Başol, *J. Appl. Phys.*, **55**, 601, (1984).

[6] Y.K. Jun and H.B. Im, *J. Electrochem. Soc.: Electrochem. Sci. Technol.,* **135**, 1658, (1988).

[7] H.S. Kim and H.B. Im, *Thin Solid Films,* **214**, 207, (1992).

[8] T. Yamaguchi, Y. Yamamoto, T. Taniska and H. Yoshida, *Thin Solid Films,* **343-344**, 516, (1999).

[9] I.O. Oladeji, L. Chow, C.S. Ferekides, V. Viswanathan and Z. Zhao, *Solar Energy Mat. and Solar Cells,* **61**, 203, (2000).

[10] J. Torres and G. Gordillo, *Thin Solid Films*, **207**, 231, (1992).

[11] T.A. Chynoweth and R.H. Bube, *J. Appl. Phys.,* **51**, 1844, (1980).

[12] S.K. Kulkarni, U. Winkler, N. Deshmukh, P.H. Borse, R. Fink and E. Umbach, *Applied Surface Sci.,* **169**, 438, (2001).

[13] T. Yamaguchi, J. Matsufusa and A. Yoshida, *Jpn. J. Appl. Phys.,* **31**, L703, (1992).

[14] T. Walter, M. Ruckh, K.O. Velthaus and H.W. Schock, Proc. 11th EC Photovoltaic Solar Energy Conf., Montreux, p. 124, (1992).

[15] M. Oztas and M. Bedir, *P.J. of Appl. Sci.*, **1**, 214, (2001).

[16] A. Kuroyanagi, *Thin Solid Films*, **249**, 91, (1994).

[17] T. Karasawa, K. Ohkawa and T. Mitsuya, *J. Appl. Phys.,* **69**, 3226, (1991).

[18] S.A. Telfar, C. Morhain, B. Urbascek, C. O'Donnell, P. Tomasini, A. Balocchi, K.A. Prior and B.C. Covenett, *J. of Crys. Growth*, **215**, 197, (2000).

[19] V. Kumar, V. Singh, S.K. Sharma and T.P. Sharma, *Optical Materials,* **11**, 29, (1998).

[20] A. Olea and P.J. Sebastian, *Solar Energy Mat. And Solar Cells,* **55**, 149, (1998).

[21] T.L. Chu and S.S. Chu, *Solid State Elec.,* **38**, 3, (1995).

[22] N. Romeo, G. Sberveglieri and L. Tarricone, *Appl. Phys. Lett.*, **32**, 807, (1978).

[23] A. Mzerd, D. Sayah, I.J. Saunders and B.K. Jones, *Phys. Stat. Sol.* **A, 119**, 487, (1990).

[24] M.P. Valkonen, S. Lindros and M. Leskela, *Applied Surface Sci.,* **134**, 283, (1998).

[25] R.S. Feigelson, A. N'Diage, S.Y. Yin and R.H. Bube, *J. Appl. Phys.,* **48**, 3162, (1977).

[26] A. Banejee, P. Nath, V.D. Vankar and K.L. Chopra, *Phys. Stat. Sol.* **A., 46**, 723, (1978).

[27] R.R. Chambedin and J.B. Bkaman, *J. of The Electro. Chem. Society,* **113/1**, 86, (1966).

[28] D. Zhou, B.F. Usher, *J. Phys: D Apply Phys.,* **34/10**, 1461, (2001).