

# Structural and optical studies on vacuum-evaporated $\text{ZnSe}_x\text{CdS}_{1-x}$ alloy films

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## Abstract

$(\text{ZnSe})_x(\text{CdS})_{1-x}$  films (about  $6\text{ }\mu\text{m}$  thick) in the entire range of  $x$  have been formed on glass substrates kept at 470 K by thermal evaporation. All the films exhibited n-type conductivity. X-ray diffraction (XRD) studies showed that films with  $0 \leq x \leq 0.70$  were polycrystalline with the wurtzite phase, whereas films with  $0.8 \leq x \leq 1.0$  crystallized in the zincblende phase. The lattice parameter varied linearly with  $x$  following Vegard's law in both the structures. The direct optical band gaps varied non-linearly, showing a downward bowing with increasing  $x$ . The bowing parameter was found to be about 0.39 eV. The structural transformation region of  $x$  obtained by analysing band gap data was found to agree well with that obtained from XRD studies.

**Keywords:** Wurtzite–zincblende; Bowing parameter; Bandgap; Alloying

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## 1. Introduction

The II–VI semiconductors with a wide range of band gap energies find potential applications in a variety of optoelectronic devices. The discrete nature of the various physical parameters and the uncontrollable microscopic and macroscopic material properties limited the use of these in a fewer devices only. Alloying of II–VI compounds can provide continuously variable parameters suitable for a number of devices. ZnSe and CdS are excellent luminescent materials and offer promising applications in devices operated in the visible spectral region. Many studies [1–4] have been aimed at producing good quality ZnSe films for their effective use in dielectric mirrors, solar cells, blue-light-emitting diodes, laser diodes and other visible luminescent devices. Bennouna and Ameziane [5] reported green edge luminescence on r.f. sputtered CdS films. ZnSe and CdS with a large band gap are efficient materials for photovoltaic heterojunctions in both thin film and bulk forms. For example an n-CdS/p-CdTe heterojunction with a solar efficiency of 8% under solar simulation of  $85\text{ mW cm}^{-2}$  has been described by Mitchell et al. [6]. According to these workers, replacing CdS by ZnSe should provide an immediate improvement in cell properties. Although

CdS and ZnSe have been investigated thoroughly, surprisingly no work has been done on the preparation and characterization of these alloys in thin film form. Even in bulk form, only structural studies are reported by Fisher and Paff [7]. These workers reported stable compositions in these alloys which is a necessary prerequisite for junction preparation. In view of the importance of this system in various device applications an attempt has been made by the present authors to investigate the thin films of ZnSe–CdS alloys with an objective of tailoring their band gap, lattice constant and other material parameters in the entire range of  $x$ . In this paper the structural and band gap are reported for the first time in thin films of the ZnSe–CdS system.

## 2. Experimental techniques

The films were deposited on Blue Star glass (India) substrates by thermal vacuum evaporation technique using a Hind-Hivac (model 12 VPM) vacuum unit. The source materials for all the compositions were prepared by first physically mixing desired quantities of 99.999% pure ZnSe and CdS (Balzers, Switzerland) and then sintering at  $1100^\circ\text{C}$  in vacuum sealed quartz

tubes for about 48 h. The  $x$  values used were 0.0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0. The deposition rates were in the range  $5\text{--}8\text{ \AA s}^{-1}$  and the films formed at 500 K. The thickness of the films was about  $0.6\text{ }\mu\text{m}$ . The chemical composition of the films was determined by the energy-dispersive X-ray analysis (EDXA) technique using an EDAX model KEVE X-ray energy analyser. Structural characterization was carried out by the X-ray diffraction (XRD) technique using a Philips X-ray diffractometer with  $\text{Cu K}\alpha$  radiation with Ni filter ( $\lambda = 1.5418\text{ \AA}$ ). The transmission spectra of the films in the wavelength range  $0.4\text{--}2.5\text{ }\mu\text{m}$  were recorded on a Hitachi U 3400 UV-visible-new IR double-beam spectrophotometer. Direct band gaps of the films were obtained by extrapolating  $(ah\nu)^2$  vs.  $h\nu$  plots to zero absorption.

### 3. Results and discussion

EDXA studies of the films revealed that all the films were nearly stoichiometric. The typical XRD patterns of  $\text{ZnSe}_x\text{CdS}_{1-x}$  films obtained in the present work are shown in Fig. 1. All the films showed a single phase with polycrystalline structure. Using analytical methods and with the help of the ASTM tables for ZnSe and CdS all the peaks were indexed. Films with  $x \leq 0.6$  were found to have a wurtzite structure whereas films with  $x \geq 0.8$  were found to have a cubic structure. In order to narrow down the structural transition region, films with  $x = 0.70$  were also prepared and used for structural studies. It was observed that films with  $x = 0.7$  were found to have a hexagonal structure. Thus it is clear that the transition region is  $0.70 < x < 0.80$ . Fig. 2 shows the variation in lattice parameter with  $x$  is linear following Vegard's law within each structure, showing complete miscibility of the compounds in both the structural phases. The figure also shows that the transition from wurtzite to zincblende is very sharp. A similar trend was reported

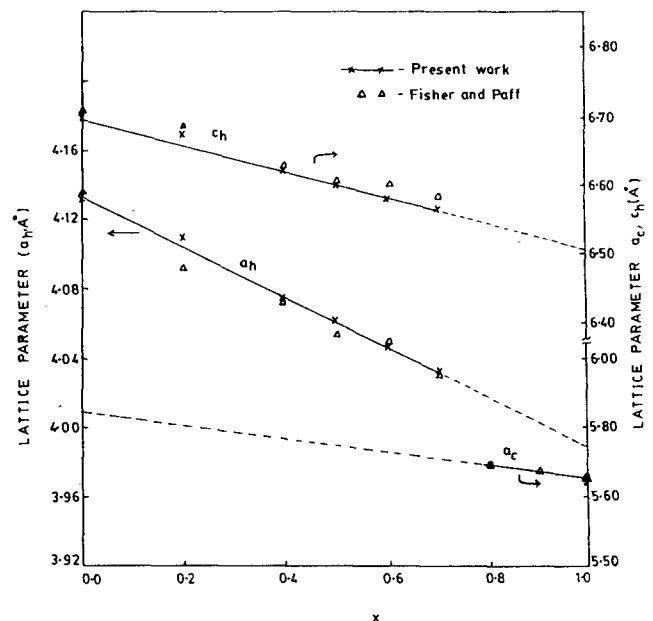


Fig. 2. Variation in lattice parameter with  $x$  for  $\text{ZnSe}_x\text{CdS}_{1-x}$  films.

for bulk alloys of this system by Fisher and Paff [7]. Such structural transitions reported earlier in other II–VI alloy systems are shown in Table 1.

From optical transmission spectra the absorption coefficient  $\alpha$  was calculated using the method followed by Neumann et al. [17]. The direct optical band gap was determined by using the formula  $(ah\nu)^2 = A(h\nu - E_g)$  for direct transitions between parabolic bands. Fig. 3 shows  $(ah\nu)^2$  vs.  $h\nu$  plots for the films with  $x = 0.2, 0.4, 0.6$  and  $0.8$ . In the present work the optical band gap is found to vary non-linearly (Fig. 4) with  $x$ , showing a downward bowing. However, Fisher and Paff [7] stated that the band gaps of the alloys lie within the range of the end compounds without giving the values and the nature of the variation with  $x$ . From the figure the bowing parameter  $b$  was found to be  $0.39\text{ eV}$ . Such non-linear variation was observed by others also for other II–VI alloy semiconductors such as  $\text{CdS}_x\text{CdTe}_{1-x}$  [13],  $\text{ZnSe}_x\text{Te}_{1-x}$  [18],  $\text{ZnS}_x\text{CdSe}_{1-x}$  [19] and  $\text{ZnTe}_x\text{CdSe}_{1-x}$  [10].

Table 1  
Structural transition regions in II–VI alloy systems

System	Structural transition region $x$	Reference
$\text{ZnTe}_x\text{CdSe}_{1-x}$	$0.40 < x < 0.50$	[8]
	$0.35 < x < 0.40$	[9]
	$0.50 < x < 0.60$	[10]
$\text{ZnSe}_x\text{CdS}_{1-x}$	$0.70 < x < 0.80$	[7]
$\text{ZnS}_x\text{CdSe}_{1-x}$	$0.60 < x < 0.80$	[11]
$\text{CdS}_x\text{CdTe}_{1-x}$	$0.35 < x < 0.50$	[12]
	$0.50 < x < 0.75$	[13]
$\text{ZnSe}_x\text{CdSe}_{1-x}$	$0.30 < x < 0.70$	[14]
	$0.40 < x < 0.60$	[15]
$\text{ZnS}_x\text{CdS}_{1-x}$	$0.60 < x < 0.80$	[16]

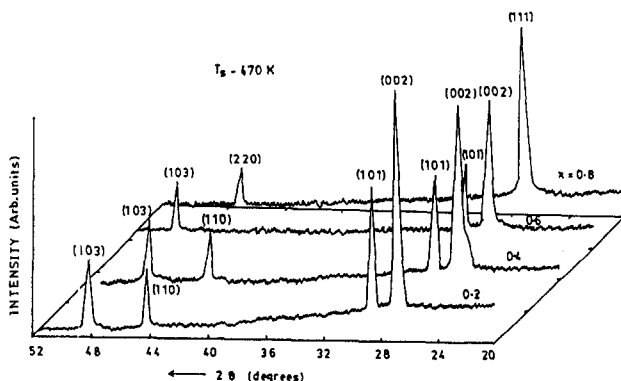


Fig. 1. XRD patterns of  $\text{ZnSe}_x\text{CdS}_{1-x}$  films for different  $x$  ( $x = 0.2, 0.4, 0.6$  and  $0.8$ ).

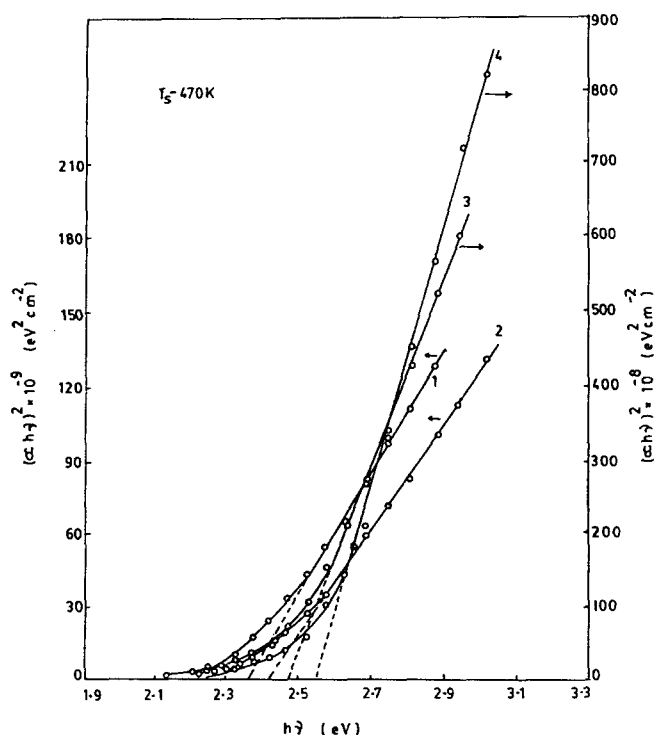


Fig. 3. Plots of  $(\alpha h\nu)^2$  vs.  $h\nu$  for different  $x$  of  $\text{ZnSe}_x\text{CdS}_{1-x}$  films: curve 1,  $x = 0.2$ ; curve 2,  $x = 0.4$ ; curve 3,  $x = 0.6$ ; curve 4,  $x = 0.8$ .

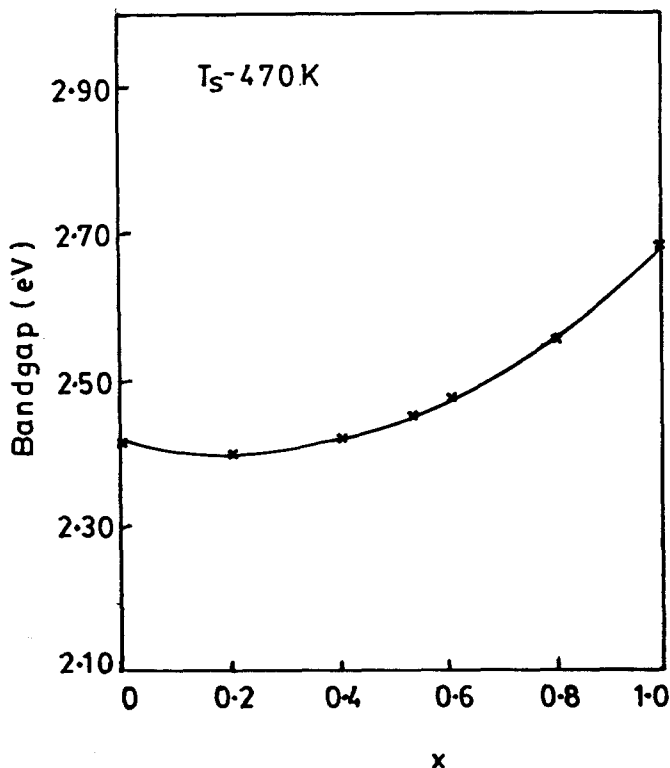


Fig. 4. The optical band gap plotted against  $x$  for  $\text{ZnSe}_x\text{CdS}_{1-x}$  films.

This kind of non-linear variation in energy gap in II–VI binary systems may be understood following Richardson and Hill [20]. According to them the

energy gap can be fitted to a quadratic equation in  $x$  of the form

$$E_g(x) = E_B + (E_A - E_B)x + bx^2$$

where  $b$  is the composition-dependent bowing parameter and gives an extent of the deviation (bowing) from linearity,  $E_A$  and  $E_B$  are the energy gaps of the end compounds A and B respectively,  $E_g(x)$  is the energy gap of the alloy of a given  $x$ -value. Further, based on pseudopotential model for II–VI binary systems consisting of end compounds with similar structures, Hill and Richardson [13] showed that  $\Delta E a^4/(1-x)$  should be constant for all values of  $x$ . On the contrary, if the end compounds have different structures, a plot of  $\Delta E_x a^4/(1-x)$  vs.  $x$  should be linear, passing through the origin. Here  $\Delta E_x = E_{\text{Lin}} - E_x$  and  $E_{\text{Lin}} = E_B + x(E_A - E_B)$ , where  $a$  is the lattice parameter of the alloy. The lattice parameters for the complementary regions are deduced from Vegard's law. The end compounds ZnSe and CdS of the present system have different structures. Following Hill and Richardson [13] a plot of  $\Delta E_x a^4(x)/(1-x)$  vs.  $x$  is made to determine the (Fig. 5) structural transformation region; it is obvious from the figure that each structure gives rise to two straight lines having different slopes. The point of intersection of these lines gives the value of  $x$  at which the structural transition is likely to take place. There is an obvious discontinuity

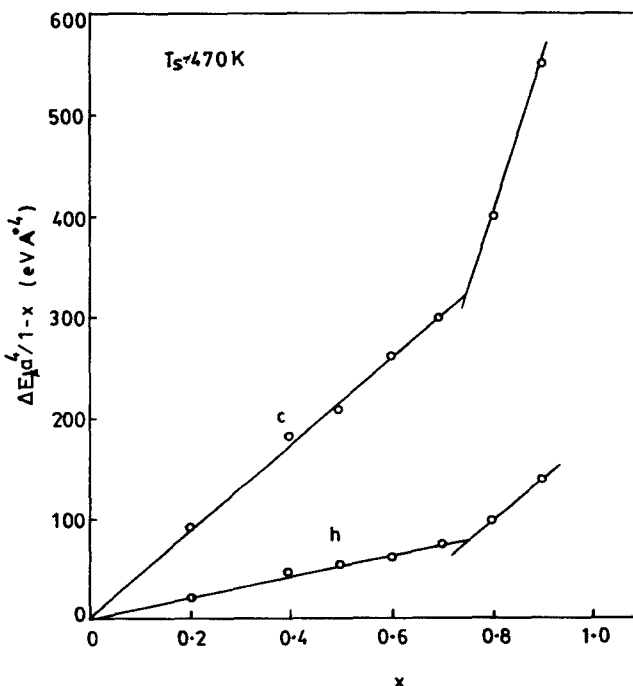


Fig. 5. Variation in  $\Delta E_x a^4/(1-x)$  with  $x$  using zincblende lattice constants for the upper line and wurtzite lattice constants for the lower line.

around  $x = 0.75 + 0.02$  where the wurtzite phase begins to yield to the zincblende phase. The XRD data also indicated a structural transition at around the same composition. Fig. 5 shows that the slope of the lower line in the zincblende stable region is the same as that of the upper line in the wurtzite phase stable region, showing that the bowing parameter depends more on the properties of the intersubstitutional atoms rather than on the structure of the lattice [20]. Fisher and Paff [7] also reported the structural transformation around  $0.70 < x < 0.80$  in bulk  $\text{ZnSe}_x\text{CdS}_{1-x}$ . There are no other data available for films of the present system for comparison.

#### 4. Conclusions

The structural transformation from wurtzite to zincblende was observed at around  $x = 0.70 < x < 0.80$  in  $\text{ZnSe}_x\text{CdS}_{1-x}$  films. The band gap varied nonlinearly with  $x$ . The lattice parameters varied linearly with  $x$  following Vegard's law in both the structures, showing that thin films of  $\text{ZnSe}_x\text{CdS}_{1-x}$  alloys are miscible in the entire range of composition. To conclude the present study indicates that the structure, lattice parameter and band gap can be tailored smoothly with composition in  $\text{ZnSe}$ – $\text{CdS}$  alloy films.

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