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Electrical properties of ZnSe–CdS alloy films

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Thin films of $ZnSe_xCdS_{1-x}$ ($t \sim 0.6$ μm) over the entire range of x, were deposited on glass substrates at two temperatures, T_s (350 and 470 K) by vacuum evaporation. X-ray diffraction studies showed that all the films were polycrystalline in nature. Films prepared at 470 K were nearly stoichiometric. Grain size increased with substrate temperature, T_s. The electrical conductivity and Hall measurements were carried out by d.c. van der Pauw technique. Hall effect studies/hot probe test showed that all the films were of n-type conductivity. Hall mobility increased with T_s. In addition, mobilities increased with temperature in films of all compositions, indicating the dominance of grain-boundary scattering. Grain-boundary potentials were in range 0.03–0.06 eV.

1. Introduction

Demand for optoelectronic chips is ever increasing and materials scientists' efforts are not in phase with this demand. Some of the demands are met by tailoring the properties through alloying the materials of known properties. Although the bulk forms are important to unearth the secrets of the nature of alloying, thin-film forms dominate in application. Some of the properties, such as structure, lattice parameter and energy gap, seem to be controllable, whereas electrical properties still remain uncontrollable in thin-film form. II–VI compounds with energy gaps covering the visible range are compatible candidates for optoelectronic chips and are extensively studied. However, only one report on the ZnSe–CdS system in bulk form [1] is available and no work is reported in thin-film form. This alloy system, with probable tailorability of energy gap and lattice parameter, is an important candidate for optoelectronic devices and tandem solar cells. The end compounds are known to show zincblende and würtzite phases and hence a phase transition in some composition range is imminent. The structure and band gap studies on the alloy system have already been communicated by the present authors [2]. These show complete miscibility and non-linear variation of band gap with composition, characteristic of substitutional alloys. In spite of autocompensation/residual trace impurities, both n- and p-type conductivities have been reported in ZnSe [3–6]. However, CdS is known to be more resilient to conductivity type change. In view of this interesting behaviour, studies on electrical properties of ZnSe–CdS alloys over the entire range of composition have been carried out and are reported here.

2. Experimental procedure

Thin films of $ZnSe_xCdS_{1-x}$ ($x = 0.0$, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0) were deposited on glass substrates (Blue Star, India) by thermal vacuum evaporation technique in a Hind-Hivac (India) (Model no. 12 VPM) vacuum coating 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 °C in vacuum-sealed quartz tubes for about 48 h. The sintered charge was slowly cooled to room temperature in about 8 h. The films were formed at 350 and 470 K substrate temperatures. The vacuum at the time of evaporation was better than 10^{-5} torr. The deposition rates were in the range 1.0–1.5 nm s^{-1} and the thickness of the films varied in the range 0.50–0.65 μm. The compositional analysis of the films was carried out by the EDAX technique using EDAX model KEVE X-7000-77 X-ray energy analyser to an accuracy of ± 5%. Structural studies were carried out by the XRD technique using a Philips pw 1130 X-ray automatic diffractometer with CuK_α ($\lambda = 0.154\,18$ nm) radiation with a nickel filter. Ohmic contacts were obtained by evaporating indium on to the films using a mica mask. The ohmic nature of the contacts was verified throughout the temperature range by the linearity of the current–voltage characteristics.

Conductivity and Hall measurements were carried out in the temperature range 150–500 K by the d.c. van der Pauw technique. The sample mounted on a copper block with electrical insulation was kept in a vacuum cryostat (10^{-4} torr). The direction of the current and the magnetic field (0.6 T) were reversed to eliminate errors due to thermo-electric and magnetic effects. Current and voltage were measured using a Philips PM 2518 X microprocessor-based multimeter and a Keithley 614 electrometer, respectively. A copper–constantan thermocouple was used for temperature measurement. The overall error in the Hall mobility, μ_H, is estimated to be ± 8%. The Hall effect studies/hot probe test were used for determination of the type of conductivity. The as-grown films had high resistivities. Annealing the ZnSe–CdS films in a hydrogen atmosphere reduced the resistivity by two to three

TABLE I Chemical composition (at %) of $ZnSe_xCdS_{1-x}$ films formed at 350 and 470 K

Composition, x	350 K				470 K			
	Zn	Se	Cd	S	Zn	Se	Cd	S
0.0	–	–	56.87	43.13	–	–	51.80	48.20
0.2	8.80	11.20	44.32	35.68	9.45	10.55	40.75	39.25
0.4	18.25	21.75	33.57	26.43	19.18	20.82	30.93	29.07
0.5	22.80	27.20	27.67	22.33	24.15	25.85	25.95	24.05
0.6	26.42	33.58	23.72	16.28	28.75	31.25	20.95	19.05
0.8	35.62	44.38	11.35	8.65	37.93	42.07	10.75	9.25
1.0	43.15	56.85	–	–	48.75	51.25	–	–

orders of magnitude. After annealing, films with $x \leqslant 0.6$ were found to be conducting and only these films were used for electrical studies.

3. Results and discussion

The estimated compositions of the constituent elements in $ZnSe_xCdS_{1-x}$ films prepared at 350 and 470 K are shown in Table I along with the target compositions. It is clear that cadmium and selenium excess and sulphur and zinc deficiencies are common in films formed at 350 K. In films formed at 470 K, the stoichiometry has considerably improved. Such deviations are common in the thin-film growth phenomenon [7]. The sticking coefficient of cadmium is higher than that of sulphur, resulting in high densities of sulphur vacancies in the films [8]. The formation of good stoichiometric CdS films was reported [9] for a substrate temperature around 473 K with a source temperature of 1123 K. Yao *et al.* [10] reported a low concentration of zinc vacancies, i.e. they obtained nearly stoichiometric ZnSe films by molecular beam epitaxy. Kuroyanagi [11] also obtained nearly stoichiometric ZnSe films by ion-beam deposition at 473 K. From Table I it is clear that nearly stoichiometric ($\pm 5\%$) films are also obtained at a substrate temperature of 470 K in the present work. Razykov [12] reported composition changes with the deposition temperature in $ZnSe_xCdTe_{1-x}$ films. Many earlier workers [13–16] have also reported better stoichiometry in II–VI compounds and their alloys formed at higher temperatures (limited temperature range). This was attributed to the increased surface mobility of atoms at higher substrate temperatures. It was shown elsewhere [2] from detailed X-ray diffraction (XRD) data that ZnSe and CdS are miscible in the entire range of composition x, and a structural transition from wurtzite to zincblende in the composition range $x = 0.7$–0.8 was observed. Typical XRDs for $x = 0.5$ are shown in Fig. 1 for two substrate temperatures. The grain sizes calculated were 37.1 and 57.4 nm for 350 and 470 K (T_s), respectively, showing that the crystallinity increases with substrate temperature. Similar behaviour was also observed in films of other compositions.

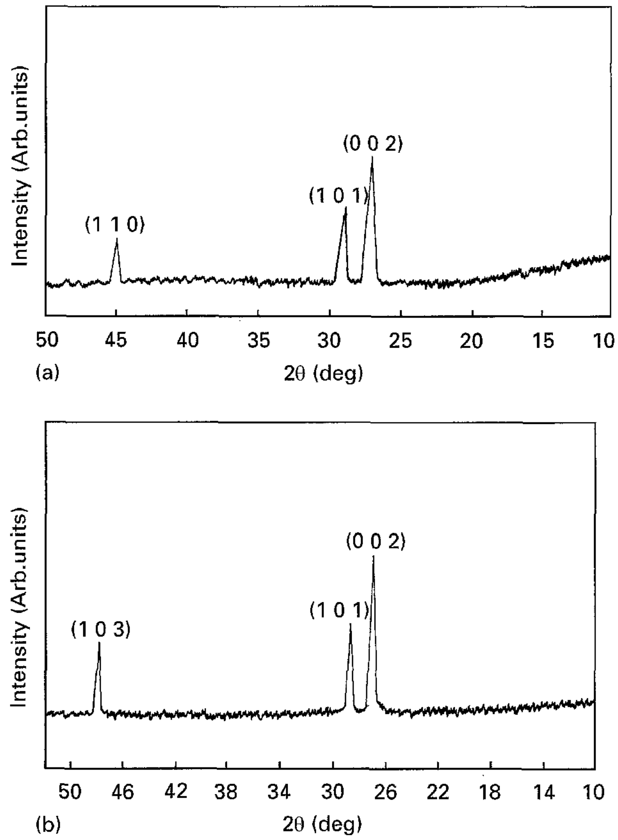

Figure 1 Typical X-ray diffractograms of $ZnSe_{0.5}CdS_{0.5}$ films. T_s: (a) 350 K, (b) 470 K.

The temperature dependence of electrical conductivity, carrier concentration and Hall mobilities of $ZnSe_xCdS_{1-x}$ films ($x = 0.2$, 0.4, 0.6) prepared at 350 and 470 K are shown in Figs 2–4. It is obvious from these figures that the conductivity increases with temperature. Table II shows typical conductivities of passivated $ZnSe_xCdS_{1-x}$ films formed at the two substrate temperatures. It is clear that films formed at 470 K are better conducting compared to films formed at 350 K. The conductivity of films of mixed compositions decreased regularly with composition x. This may be attributed to the increase in the electron binding energy with increasing ZnSe content, because ZnSe has more electron binding energy than that of CdS. The conductivity plots show two activated regions in the temperature range studied. The activation energies in the low- and high-temperature regions are given in Table II. The high-temperature activation energy is higher in films of all compositions. No regular variation of conductivity activation energy with composition is observed. It is also not possible to associate the activation energy with any physical pro-

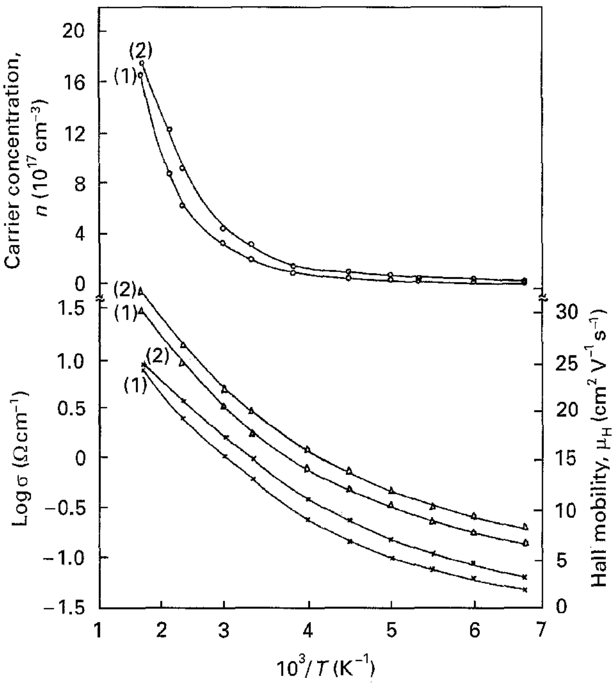

Figure 2 Variation of (×) electrical conductivity, σ, (○) carrier concentration, n, and (△) Hall mobility, μ_H, with temperature for $ZnSe_{0.2}CdS_{0.8}$ films. T_s: (1) 350 K, (2) 470 K.

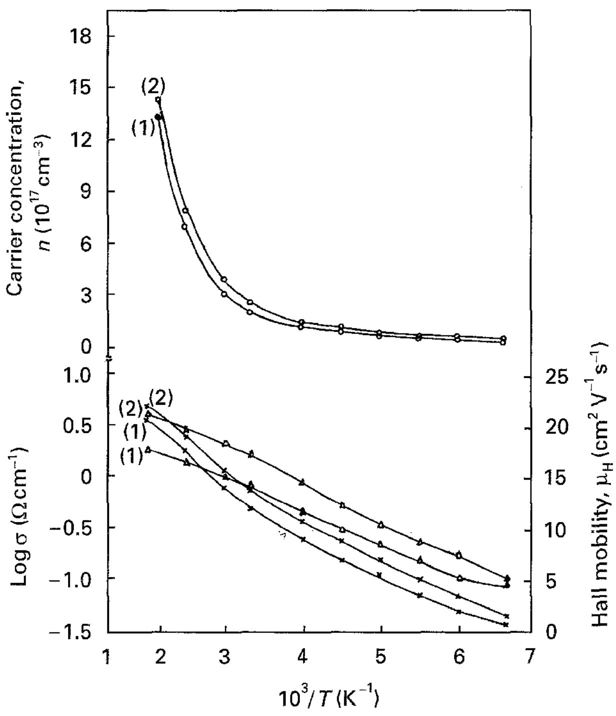

Figure 3 Variation of (×) electrical conductivity, σ, (○) carrier concentration, n, and (△) Hall mobility, μ_H, with temperature for $ZnSe_{0.4}CdS_{0.6}$ films. T_s: (1) 350 K, (2) 470 K.

cess, because conductivity is a function of both mobility and carrier concentration.

The Hall mobilities of carriers at 150 and 500 K in $ZnSe_xCdS_{1-x}$ films formed at 350 and 470 K are given in Table III. It is clear that the carrier mobilities in films formed at higher temperature are comparatively higher. This is due to better crystallinity and stoichiometry of the films formed at 470 K. Further, the high-temperature mobilities are higher than the

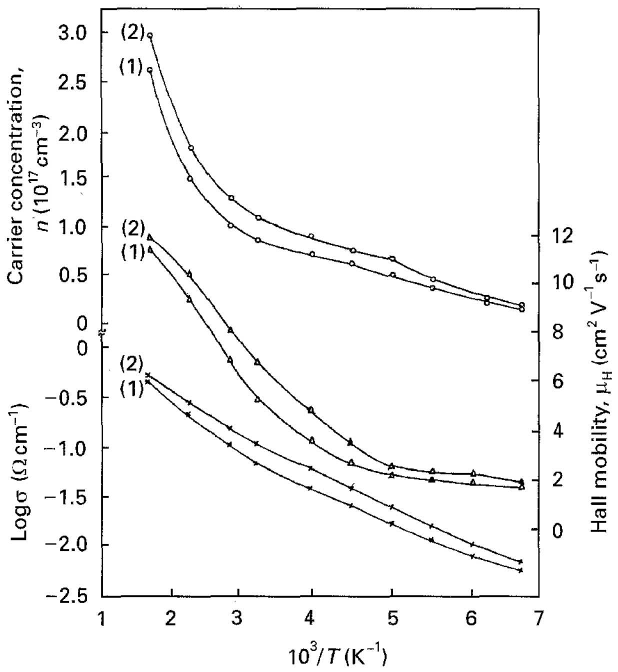

Figure 4 Variation of (×) electrical conductivity, σ, (○) carrier concentration, n, and (△) Hall mobility, μ_H, with temperature for $ZnSe_{0.6}CdS_{0.4}$ films. T_s: (1) 350 K, (2) 470 K.

low-temperature mobilities in films formed at both the substrate temperatures. A similar increase in mobilities with temperature and with T_s was reported by Kowk and Siu [17] in CdS films. The mobility does not show any regular variation with composition x. Such irregular variation was observed in $ZnTe_xCdSe_{1-x}$ single crystals also by Venugopal *et al.* [18]. This may be due to the unknown preparation conditions and the defect structure which influence the electrical properties to a large extent. The room-temperature mobilities obtained in the present work in $ZnSe_xCdS_{1-x}$ $(0 \leqslant x \leqslant 0.6)$ alloy films are in the range 5.69–19.75 $cm^2 V^{-1} s^{-1}$ (T_s = 470 K) and these are within the range of values reported by earlier workers in CdS films [19, 20].

In the present films, the mobility increased with temperature (Figs 2–4) indicating the dominance of grain-boundary scattering. The models of Seto [21] and Baccarani *et al.* [22] have been successfully used for calculating the grain-boundary potentials in polycrystalline silicon with known (doped) amounts of impurities/trapping levels. II–VI compounds are fully compensated and a knowledge of defect concentration structure and the trapping levels at the grain boundaries is necessary for obtaining grain-boundary potentials using the above models. In the absence of these data, the formula of Waxman *et al.* [23] given by

$$\mu_{gb} = \frac{e3^{1/2}}{4N(kT)^{1/2}}\exp(-e\phi_{gb}/kT) \qquad (1)$$

has been successfully used for calculating the grain-boundary potential in CdS films [24, 25]. Here e is the charge of the electron, k is the Boltzmann constant, T is the absolute temperature and m^* is the effective mass of the electron. N is the number of grains and ϕ_{gb} is the grain-boundary scattering potential. In the

TABLE II D.C. conductivity and conductivity activation energies of $ZnSe_xCdS_{1-x}$ films prepared at 350 and 470 K

Composition, x	Conductivity, σ ($\Omega\,cm^{-1}$)				Activation energies (eV)			
	350 K		470 K		350 K		470 K	
	160 K	500 K	160 K	500 K	A[a]	B[b]	A[a]	B[b]
0.0	0.047	5.88	0.063	7.08	0.066	0.180	0.078	0.168
0.2	0.052	7.94	0.087	9.44	0.023	0.205	0.071	0.155
0.4	0.039	3.75	0.047	5.01	0.054	0.129	0.069	0.122
0.5	7.94×10^{-3}	0.56	6.60×10^{-3}	0.89	0.052	0.104	0.081	0.102
0.6	6.68×10^{-3}	0.47	7.91×10^{-3}	0.56	0.058	0.119	0.065	0.109

[a] Low-temperature region.
[b] High-temperature region.

TABLE III Hall mobility, μ_H, carrier concentration, n, carrier activation energies, ΔE, of $ZnSe_xCdS_{1-x}$ films prepared at 350 and 470 K

Composition, x	μ_H ($cm^2\,V^{-1}\,s^{-1}$)				n ($10^{17}\,cm^{-3}$)				ΔE (eV)	
	350 K		470 K		350 K		470 K		350 K	470 K
	150 K	500 K	150 K	500 K	150 K	500 K	150 K	500 K		
0.0	5.08	27.26	7.53	28.40	0.59	14.2	0.49	15.91	0.081	0.104
0.2	6.71	29.87	8.25	31.73	0.52	16.6	0.54	17.55	0.112	0.103
0.4	4.81	17.75	5.02	21.25	0.52	13.4	0.60	14.42	0.084	0.081
0.5	0.75	7.63	0.68	8.82	0.65	4.6	0.62	6.31	0.044	0.087
0.6	1.70	11.11	1.84	11.68	0.25	2.6	0.27	3.00	0.036	0.037

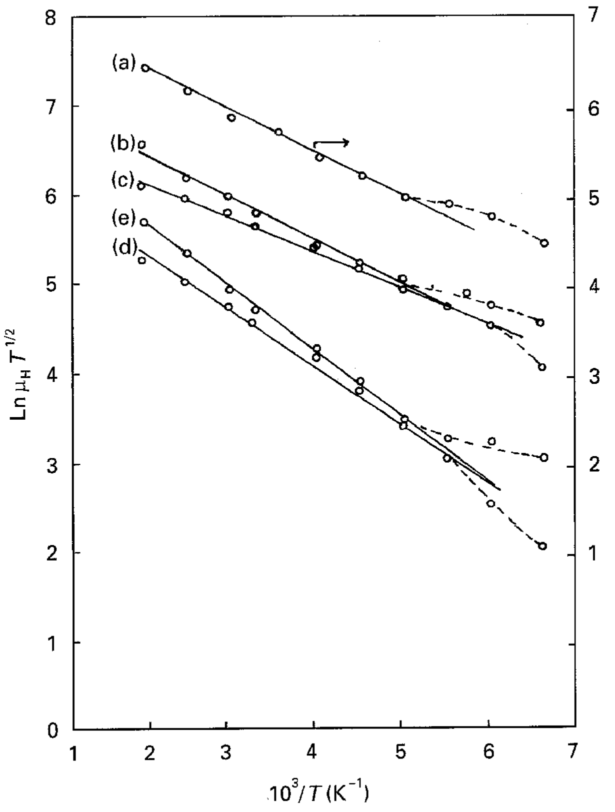

Figure 5 Variation of $\ln \mu_H T^{1/2}$ with $1/T$ for $ZnSe_xCdS_{1-x}$ films. x: (a) 0, (b) 0.2, (c) 0.4, (d) 0.5 and (e) 0.6 $T_s = 470$ K.

present work also, the same expression is used. Plots of $\ln \mu_H T^{1/2}$ versus $1/T$ are shown in Fig. 5. The grain-boundary potentials, ϕ_{gb} calculated from the slopes of these plots, lie in the range 0.034–0.060 eV and are 0.043, 0.043, 0.034, 0.053 and 0.060 eV for films with $x = 0.0$, 0.2, 0.4, 0.5 and 0.6, respectively. The grain-boundary potential varies irregularly with x. This might be due to the preparation conditions that control the grain boundaries other than the composition, x, in $ZnSe_xCdS_{1-x}$ films. Grain-boundary scattering has been reported by other workers [20, 25, 26] also in CdS films. However, Dawar *et al.* [27] reported the dominance of acoustic phonon scattering in the temperature range 100–300 K in vacuum-evaporated CdS films deposited at 423 K. Their mobility data decreased with temperature in accordance with the relation $\mu_H \propto T^{-1.52}$.

Hot-probe test/Hall effect studies showed that the majority charge carriers are electrons (n-type) in films of all compositions. This strong tendency towards n-type conductivity is attributed to autocompensation, the presence of residual impurities [28, 29]. In II–VI compounds, the native defects are even doubly ionized and the autocompensation is as much as 90% [29]. This is mainly due to comparable magnitudes of the energies of formation of the native defects and the energy gaps of II–VI compounds. Further, it was shown by Mandel *et al.* [30] that if the ratio R_M/R_N of anion (M) and cation (N) radii is less than 1.06, only p-type conductivity is possible. If this ratio lies between 1.06 and 1.12, both types of conductivity are possible and beyond 1.12 only n-type conductivity is possible. The covalent radii ratios of ZnSe and CdS are 1.15 and 1.42, respectively. Therefore, the observed type of conductivity in the present films is justified. However, a critical analysis of single crystalline films data on ZnSe does not seem to support the autocompensation concept, and the type of conductivity may be attributed to trace impurity atoms. These arguments hold good only for thermodynamically reversible systems and the reports of complementary conductivities in non-equilibrium state are not uncommon in II–VI semiconductors [29]. The n-type conductivity observed in the present alloy films is either due to autocompensation or due to trace impurities which are not analysed in the present investigation.

From Figs 2–4 it is clear that the carrier concentration increases with temperature for films of all compositions. In general, the carrier concentrations in films formed at 470 K are higher compared to those in films formed at 350 K. The carrier concentration in CdS films was reported to be of the same order by Kolhe *et al.* [31], Kowk and Siu [17] and Uda *et al.* [32]. The present carrier activation energies are in the range 0.036–0.112 eV in films formed at 350 K and 0.037–0.104 eV in films formed at 470 K. These activation energies are not found to vary regularly with composition.

4. Conclusion

Higher substrate temperature improved the stoichiometry and crystallinity of the films. Conductivity decreased with increase in ZnSe content and is attributed to stronger binding of electrons in ZnSe than in CdS. The Hall mobility is limited dominantly by the grain-boundary scattering with the grain-boundary potentials lying in the range 0.034–0.060 eV. The conductivity type is decisively n-type over the entire composition range and is attributable to autocompensation/residual impurities.

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