

PREPARATION AND CHARACTERIZATION OF ZnSe:Al THIN FILMS

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Thin films of ZnSe:Al were deposited on glass substrates by laser assisted evaporation. Parameters such as crystal structure, optical and electrical properties of the films have been investigated. X-ray diffraction shows that prepared films are polycrystalline with preferred (111) orientation and having a zinc blend cubic structure. The lattice constant has been evaluated for ZnSe, the value was found to be 0.56 nm, and the value does not show any appreciable change with the addition of aluminium. From optical measurement, it was found that optical band gap, E_g , decreases on adding Al. The value changes from 2.62 eV (for ZnSe) to 1.85 eV with 3.0 wt % of Al in the film. Hall effect measurements showed that the films are all n-type and the carrier concentration increases with the increase of Al concentration in the film. DC electrical conductivity may be thermally activated with negligible activation energy only when the Al concentration is lower than 3 wt % at temperature up to 200° C, and the transport process may involve hopping of electrons in the localized states near the conduction band edge. However, at higher concentration of Al the process is dominated by usual transition of electrons to the mobility edge. Addition of Al up to 3 wt % does not only increase the electrical conductivity by a factor of 10^2 but also the carrier concentration by a factor of 10^3 which may bring about electron degeneracy at room temperature by dislodging the Fermi level.

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1 Introduction

Zinc Selenide (ZnSe) is a wide band gap II-VI semiconductor and has attracted considerable attention for their wide range of applications in various optoelectronic devices and in solar cells. It is a direct band gap semiconductor and is transparent over wide range of visible spectrum. Polycrystalline ZnSe thin films have been identified as suitable material for electroluminescent display and window layers in solar cells. In recent years, considerable efforts have been devoted to develop blue green laser diodes based on ZnSe and its alloys. So far these have not been realised, mainly because of the difficulty in controlling electrical conduction. Preparation of

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conductive layer is essential for its use as light emitting devices. As in other large band gap semiconductor systems, progress in ZnSe was hindered by the lack of shallow dopant sources, essentially acceptors. To obtain low resistivity n-type ZnSe group-III elements such as Al and Ga and group-VII element Cl₂ has been tried [1–3]. A number of attempts have also been made to grow p-type ZnSe [4, 5] specially doping with nitrogen, however it was found to be difficult to grow films with higher carrier concentration. Recently p-type doping becomes successful through plasma activated N doping [1]. However, problem arises in controlling the stoichiometry of the film deposited. Zinc vacancy is a major defect that compensates for all extrinsic dopants. This restricts the ability to obtain films with lower resistivity that limits its extensive applications. Recently single-phase layer of sulphur doped ZnSe films have been deposited by spray method for photovoltaic applications [6].

Various methods have been used for the growth of ZnSe thin films. Most frequently used methods are molecular beam epitaxy (MBE) [2, 7] thermal evaporation [8] organo-metallic chemical vapour deposition (OMCVD) [1, 9] closed spaced vapour transport (CSVT) [10] liquid phase epitaxy (LPE) [11] gas transport (GT) [12] and pulse laser deposition.

Laser assisted evaporation has also been used as a thin film deposition technique [13, 14] for long and found to possess several advantages over other techniques. This technique utilizes the energy of a laser to vaporize a source material. In this respect, it is similar to electron beam evaporation except that in this case, the power source is outside the vacuum system, and the depth up to which the incident energy is absorbed varies from a few hundred angstroms to several millimetres depending on the material properties and laser wavelength.

So far no detail investigations have been made on ZnSe:Al thin films. In this paper we have reported the preparation and characterization of ZnSe:Al thin films deposited by cw (continuous wave) CO₂ laser assisted evaporation. Results of the structural, optical and electrical properties have been presented and discussed.

2 Experimental details

ZnSe:Al thin films have been deposited on optically polished glass substrates at 250° C by cw CO₂ laser assisted evaporation. Samples were prepared by adding up to 3.0 wt % of Al with ZnSe. Substrates used for film deposition were glass and were cleaned properly by first cleaning them with a detergent and then with de-ionised water. They were then treated with methanol. Finally, they were cleaned ultrasonically by dipping them in acetone.

The starting materials used for the preparation of films were ZnSe granules (purity 99.999%) and aluminium powder (99.9% purity) obtained from Belzer U.S.A. ZnSe granules were made powder and then mixed thoroughly with Al by using mortar and pestle. Pellets of 5.0 mm thick and 13.5 mm diameter were made under high pressure using Parkin Elmer equipment. Pellets were then placed on a target approximately 5.0 cm away from the substrate holder for evaporation. The assembly was placed in a vacuum chamber and the chamber was then evacuated to $\approx 1.33 \times 10^{-4}$ Pascal before turning on the laser source. Different laser powers were tried and different substrate temperatures were used to produce good and uniform films. To improve the uniformity of growth a slow oscillatory motion was given to the substrate holder connecting it with a motor placed outside the vacuum chamber. The position of the laser beam striking the target was also varied using a handle attached to the target holder to erode the source pellet more

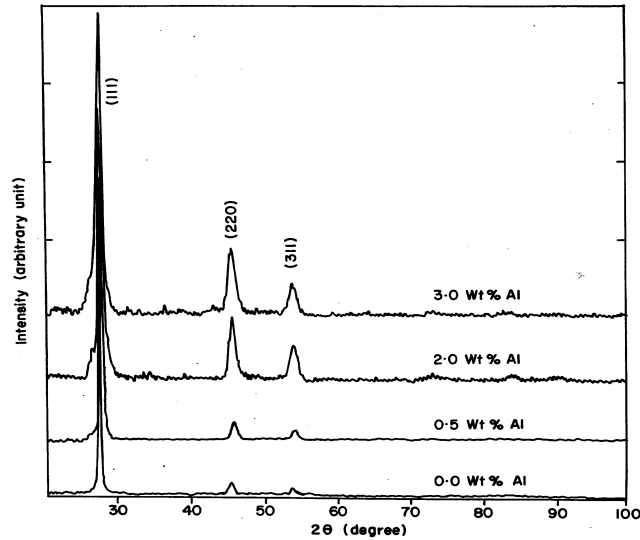


Fig. 1. X-ray diffraction spectra for ZnSe:Al thin films.

uniformly and to stimulate a larger area of the surface for achieving better uniformity of the deposited film.

In the deposition processes, it was observed that in some cases films had the tendency to peel off from the glass substrates after long exposure to air. Annealing the film in air immediately after deposition above the substrate temperature for an hour made them stable, adhere well and do not peel off from the glass substrates. Similar result was obtained when the films were annealed in situ for an hour after the deposition.

The thickness of the films grown under the condition mentioned was found to be about 0.7-0.8 nmsec^{-1} and typically, films of about 800 nm were obtained. The thickness of the films was measured using an alpha step-200 instrument. Crystal structures were determined by taking x-ray diffraction (XRD) on a Siemens D500 diffractometer. Optical transmission and reflection in the range 0.2-1.0 μm were taken with a Hitachi U3210 spectrophotometer. The electrical properties were measured by van-der Pauw's four-point probe method using silver paste for making ohmic contact of electrode with the films.

3 Results and Discussion

3.1 Structural Properties

X-ray diffraction analysis was performed on ZnSe:Al to ascertain the crystal orientation and the structure of the materials deposited. XRD spectra were taken using $\text{Cu K}\alpha$ radiation on films deposited at 250° C. Fig. 1 shows the spectra obtained on films containing different concentration of Al.

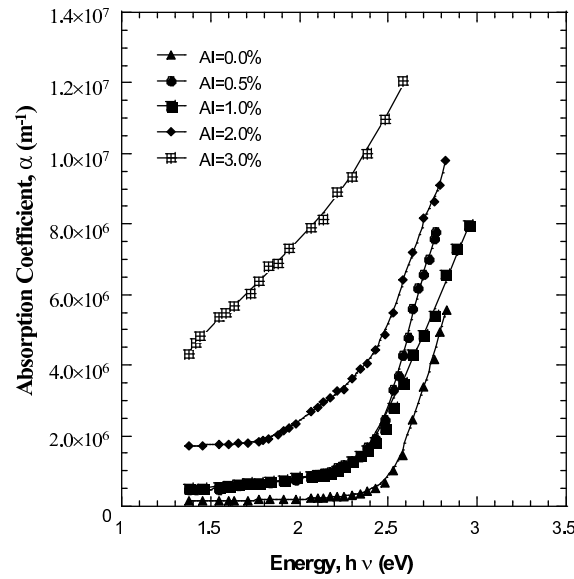


Fig. 2. Variation of absorption coefficient with photon energy for ZnSe:Al thin films.

It can be seen from the figure that the films are of polycrystalline nature having (111) preferred orientation and exhibiting a zinc blend cubic structure. The traces also indicate that the main and the most intense peak occur at $2\theta = 27^\circ$ and it corresponds to the (111) orientation. It is the dominant peak in all spectra. In addition to this peak, there are also peaks at 45.2° and 53.8° corresponding to (220) and (311) orientations respectively. In every spectrum, the absence of any hexagonal reflection from (100), (101), (102) and (103) planes confirms the formation of single-phase material that is obtained from the laser-assisted evaporation. The lattice constant of ZnSe evaluated from the diffraction pattern is ≈ 0.56 nm. This value is slightly smaller than the value reported by other workers from their x-ray analysis of ZnSe [15, 16]. From Fig. 1 it is also observed that spectrum of the films containing Al (up to 3 wt %) do not show any additional peak other than those appeared for ZnSe. This indicates that the Al atoms have made solid solution with ZnSe by replacing Zn atoms or by occupying any Zn vacancy in the lattice. It is also observed that as the Al concentration increases the intensity of the main (111) peak gradually decreases and those of the minor peaks increase and there occurs a very small shift of the position of the peaks towards the higher angle of diffraction. The decrease in intensity of (111) peak and small shift of the peaks may be interpreted in terms of the atomic scattering factor [17].

3.2 Absorption coefficient and optical band gap

The optical absorption coefficient of ZnSe:Al thin films were investigated using the optical transmittance spectra in the range 0.2 to $1.0 \mu\text{m}$. It was found that films are highly transparent. The absorption coefficient α at different photon energy has been calculated using the relation

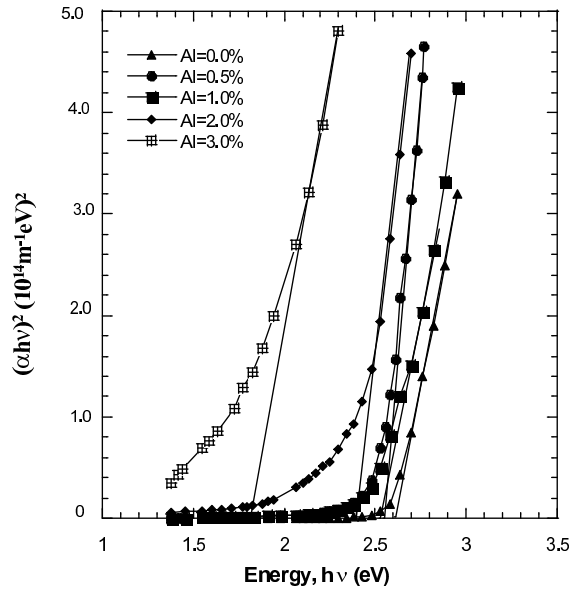


Fig. 3. Plot of $(\alpha h\nu)^2$ versus photon energy $h\nu$ for ZnSe:Al thin films.

$T = A \exp(-\alpha t)$, where T is the transmittance, t is the thickness of the films and A is a constant. The variation of absorption coefficient α with photon energy of the films deposited at 250° C is shown in Fig. 2.

It is observed from the figure that α increases exponentially with photon energy. The value also increases with aluminium concentration. Fig. 2 also shows that the absorption edge is quite sharp for film without Al but as Al concentration increases the absorption edge becomes less and less sharp. This is an indication that the crystal is becoming more disordered as Al is added in ZnSe lattice. The grain boundaries of the disordered films normally act as sinks for impurities and may give rise to a marked contribution to the optical absorption and hence films containing Al has higher absorption coefficient. The increase in disorder may also be responsible for the decrease in the intensity of (111) peak of the XRD, as observed in Fig. 1.

The optical absorption coefficient in a semiconductor can be given by a simple relation [18]

$$\alpha = \frac{A(h\nu - E_g)^m}{h\nu}, \quad (1)$$

where A is a constant and E_g is the optical band gap. In the fundamental absorption region of the spectra the qualitative nature of optical transition is determined by the value of m . Considering $m = 1/2$ for direct and allowed transition of carriers across the gap a few plots of $(\alpha h\nu)^2$ as a function of $h\nu$ for ZnSe:Al are shown in Fig. 3 where the samples with Al composition from 0 to 3.0 wt % are presented.

The observed linear dependence of $(\alpha h\nu)^2$ on $h\nu$ in the higher absorption side of the spectra, as shown in this figure, confirms that ZnSe:Al has a direct band gap. The values of E_g have been

calculated by extrapolating the linear region of the curves to $(\alpha h\nu)^2 = 0$. It is also clear from the figure that the optical band gap gradually decreases with increasing aluminium composition. The value decreases from 2.62 eV (ZnSe without Al) to 1.85 eV (ZnSe with 3.0 wt % of Al). The nature of variation of E_g with Al concentration in ZnSe film is shown in Fig. 5. We observe a clear shift of the absorption edge towards a lower energy due to the addition of Al dopant.

The shift of absorption edge with the addition of dopants in semiconductors is a remarkable effect and is observed in many compound and oxide semiconductors [18, 20]. In the present case, due to gradual addition of Al in the lattice the conduction band density of states function is perturbed due to many body effects on the bands, which may shift the Fermi level towards the conduction band edge and produce considerable band tailing in the gap region. At the same time the built-in electric field of the ionized donors in these films can also produce band gap shifting via Franz-Keldysh effect (F-K) when the doping concentration is higher than 2 wt %. We have estimated the generated electric field in our ZnSe:Al films those have higher Al doping. The field is about 10^8 Vm^{-1} while the optimum field for F-K effect is $\approx 10^7 \text{ Vm}^{-1}$. There is of course some smearing effect due to local deformation of the lattice brought about by randomly introduced Al ions and ionic size mismatch of Al^{3+} and Zn^{2+} . The latter can affect the band gap for each microcell of the crystal. In this situation the band gap should be statistically distributed around the mean value of pure ZnSe film. We therefore see that there is finite probability of tunnelling of conduction band Bloch states into the band gap due to several reasons as mentioned above and resonance optical absorption may take place at energies $h\nu < E_g$ showing band gap narrowing.

3.3 Electrical Properties

Hall effect and resistivity of ZnSe:Al thin films deposited at 250°C and with Al concentration up to 3 wt % were measured at room temperature. Electrical resistivity was also measured from room temperature to 200°C . Hall mobility and carrier concentrations have been determined from Hall effect measurements and it is found that all the films are n-type. Resistivity of the samples decreases with the increase of temperature showing a negative temperature coefficient. Depending on the Al concentration resistivity decreases from 0.658 to $0.4 \times 10^{-2} \Omega\text{m}$, and carrier concentration increases from 10^{22} to 10^{25} m^{-3} with the addition of 3 wt % Al. Values of resistivity and the carrier concentration are shown in table 1. Similar results were reported for I-doped ZnSe films prepared by metallorganic vapour phase epitaxy [21].

Figure 4 shows the temperature dependence of dark conductivity, σ , of ZnSe:Al samples (Al = 0.5 to 3.0 wt%). For all the samples, plots of $\ln \sigma$ versus $1000/T$ are almost linear and the nature of variation of σ with T does not correspond to any substantial activation of carriers in the investigated temperature range. Films with 0.5% Al show a slight activation in the temperature range 140°C - 180°C , and films with higher concentration of Al do not show remarkable variation of σ with T . The slight activation, which is present, has been calculated using the relation [18]

$$\sigma = \sigma_0 \exp\left(\frac{\Delta E}{k_B T}\right), \quad (2)$$

where σ_0 is the pre exponential factor indicating high temperature limit of σ or when ΔE vanishes. ΔE is the so called activation energy for dc conduction and k_B is the Boltzmann constant. Using Fig. 4 and equation (2) the values of σ and ΔE for the set of samples have been calculated

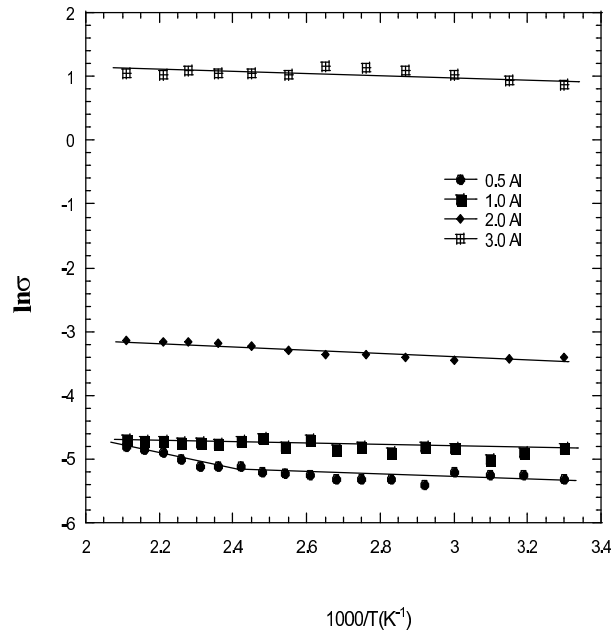


Fig. 4. Variation of $\ln \sigma$ with $1000/T$ for ZnSe:Al thin films.

and are given in Table 1. It is seen from the values of the activation energies that the impurity levels lie very close to the conduction band. At 3 wt% of Al it seems that this level may have some overlap with the band tail since $\Delta E < k_B T$ at room temperature. In this situation the current is carried out by electrons excited to the mobility edge E_c and $\Delta E = E_c - E_F$ where E_F is the Fermi level. On the other hand, at room temperature the possibility of electron hopping among the localized donor states (at the lower Al concentrations in the samples) cannot be overruled. It has to be remembered that ΔE is actually a concentration dependent parameter, as we observe here, and hopping is a phonon assisted tunnelling mechanism.

Tab. 1. Different parameters observed for ZnSe:Al thin films

Al-conc wt %	Optical band gap E_g / (eV)	Resistivity $10^{-2} \Omega m$	σ (Ωm) $^{-1}$	Carrier conc. / (m^{-3})	ΔE eV
0.0	2.62	65.8	1.5	1.03×10^{22}	
0.5	2.55	62.4	7.2	1.8×10^{22}	0.0392
1.0	2.50	56.7	7.5	4.5×10^{22}	0.0375
2.0	2.42	27.4	11.8	3.0×10^{22}	0.0308
3.0	1.85	0.4	3.3×10^2	4.8×10^{25}	0.0072

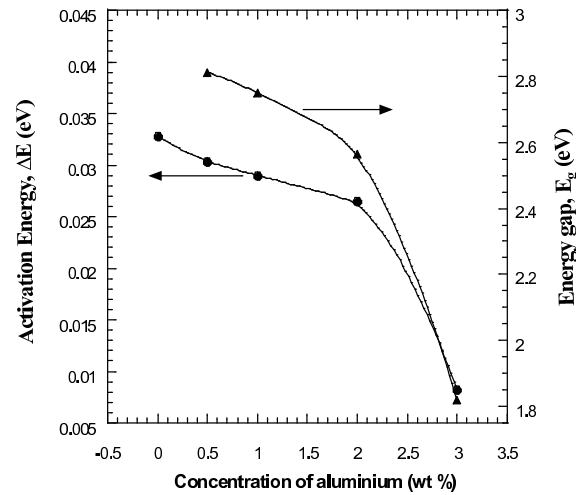


Fig. 5. Variation of activation energy and band gap of ZnSe:Al thin films with Al concentration.

The variation of activation energy ΔE with Al concentration is shown in Fig. 5. From this figure it is observed that ΔE decreases gradually with the increase in Al concentration up to 2 wt % and then very rapidly at higher concentrations. As we notice that, the carrier concentration also increases correspondingly in this region. This can broaden the donor states to form an impurity band just near the conduction band. The increase of conductivity due to higher Al doping, as can be noticed in Fig. 4, is a consequence of higher carrier supply in the film which can raise the Fermi level towards the appropriate mobility edge E_c . Similar type of results have been reported for some impurity doped Chalcogenide glasses elsewhere [22, 23].

4 Conclusion

ZnSe:Al thin films were deposited by cw CO₂ laser assisted evaporation method onto optically polished glass at 250° C using different wt % of Al. Films deposited are found to be polycrystalline having cubic Zinc blende structure with (111) preferred orientation. Optical band gap decreases on adding aluminum with ZnSe. From resistivity and Hall effect measurements it was found that films prepared are of n-type. The carrier concentration increases with increasing Al concentration and the value obtained with 3.0 wt % of Al is $4.8 \times 10^{25} \text{ m}^{-3}$. The dc conductivity shows that within a temperature range up to 200° C only one type of conduction mechanism is involved when the doping level is high. The activation energy decreases with the increasing Al concentration. The low values of activation energy suggests that the conduction may take place by electron hopping in the impurity band in some of the films with lower concentration of Al. While at higher concentrations of doping some overlap of the donor states with the delocalised tail states in the band gap may initiate electron degeneracy at room temperature. It is reasonable to mention here that the onset of degeneracy and narrowing of band gap both are related to concentration dependent density of states function.

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