ABSTRACT

ZnSe, an important II–VI compound semiconductor, has been drawing considerable research interest due to its potential application in blue-green lasers, light emitting diodes, optically bistable devices, solar cells, dielectric mirrors and filters, etc. In these device applications, epilayers and thin films are fast replacing single crystals. The use of thin films of ZnSe is an economically viable approach in the production of heterojunction solar cells, optical coatings and transistors. For the sake of optimal performance, these films should have specific mechanical, optical and electrical properties. Film microstructure including stoichiometry have considerable effect on the above-mentioned properties. For deposition of high quality polycrystalline films at relatively low cost, vacuum evaporation is one of the most convenient methods.

In view of the above-mentioned facts and considering the lack of systematic study of physical properties of evaporated ZnSe films, the purpose of the present study was to investigate the correlation of microstructural, optical and electrical properties of polycrystalline ZnSe thin films. The following thesis describes our effort towards the deposition of ZnSe thin films on glass substrates by vacuum evaporation method from bulk ZnSe synthesized at laboratory; structural characterization of the films by X-ray diffraction (XRD) method, energy dispersive X-ray (EDX) analysis and scanning electron microscopy (SEM); optical characterization by spectrophotometric measurements and preliminary electrical characterization of the films and lastly to present an interrelation among microstructural, optical and electrical properties of ZnSe thin films.

Bulk ZnSe powder was synthesized in the laboratory from specpure (99.999%) zinc and selenium powder (mixed in atomic weight ratio 45.292 : 54.708) by heating at 1273 K in an evacuated and sealed graphite-coated quartz tube. The powdered ZnSe was analyzed by X-ray diffraction technique and the diffraction lines thus obtained from the prepared sample were in good agreement for their values of relative intensity and interplaner spacing with the standard values for pure ZnSe.

ZnSe thin films were deposited on clean microglass slides by vacuum evaporation of ZnSe powder synthesized in laboratory. Prior to deposition, the slides were cleaned properly. The source and substrate temperatures were measured with chromel-alumel thermocouples. The evaporation source was a small quartz tube (ID 3 mm) heated by passing current through tungsten wire basket. The substrate temperature was varied through $T_{sub} = 300\,\mathrm{K}$ (room temperature), 373 K, 473 K and 573 K. The source temperature was kept at 1143 K with vacuum system pressure at 3×10^{-6} Torr and the source-to-substrate distance was fixed at 10 cm in all the depositions.

The thickness of ZnSe film was measured from interference maxima and minima of transmission spectrum recorded by a double-beam UV-VIS-NIR spectrophotometer (Shimadzu UV2100) and they were in the range 250–500 nm. The bulk composition of the films was determined by energy dispersive X-ray (EDX) analysis using Cam Scan IIDV series electron microscope with Link AN10000 superseries AN10/555 EDX microanalysis system at accelerating potential of 15 kV. The surface morphology of the films were studied by scanning electron microscope (SEM) (Cam Scan series IIDV) operated at 10 kV.

Structural characterization was done by a X-ray diffractometer (Philips PW1840) applying line broadening analysis. Optical transmittance ($T\%$) and absorbance (ABS) measurements were done on the films in wavelength range 350–900 nm by above-mentioned spectrophotometer at room temperature. The electrical conductivity (σ) of these films was measured by two-probe method with an electrometer (Keithley 602 solid state model) having input impedance 10^{14} ohms shunted with 20 picofarad. Appropriate electrical contacts were made applying thin layers of silver paste and a system for temperature variation was also attached. As the films were highly resistive, the whole set-up was guarded for pick-ups. The conductivity type was measured by Seebeck effect experiment with films having length to breadth ratio 5 : 1.

XRD line profiles of ZnSe thin films deposited at different substrate temperatures showed a sharp single peak corresponding to (111) preferred orientation. However no other peak with measurable intensity from either ZnSe or the elemental constituents or their oxides was obtained in the X-ray diffraction trace. This proved that the ZnSe thin films were polycrystalline with zinc blende structure.

In the compositional analysis of ZnSe thin films by energy dispersive X-ray (EDX), the normalized values of Zn and Se were calculated for atomic percentage determination. The ZnSe thin films were generally zinc deficient. But we found that the film stoichiometry improved greatly with increasing substrate temperature.

ZnSe thin films deposited at and below 373K did not stick well to the glass substrates whereas films adhered to the glass slides when grown at 473K and 573K. The lattice parameter and average internal stress of ZnSe thin films were determined from peak positions of XRD profile, while the grain size, lattice strain and dislocation density of the films were calculated by integral width determination of the XRD profiles. The background level had been taken to be the mean of the two minima adjacent to the peak and was adjusted for all the films properly.The pure integral width β was used to obtain the grain size D and lattice strain ϵ assuming an exclusive contribution to broadening for either grain size or lattice strain. The dislocation density ρ was calculated using the grain size and lattice strain values.

The lattice parameter of ZnSe thin films first increased abruptly and then decreased to some extent with increase in substrate temperature. The average internal stress of ZnSe thin films was tensile for room temperature (300 K) deposited films, but it changed to compressional stress—first increasing, coming to a peak and then decreasing nominally as films were deposited at increasing substrate temperature.

The grain size increased first abruptly and then slowly for increase in T_{sub}, while both lattice strain and dislocation density followed opposite behaviour—decreasing first abruptly and then slowly for increase in T_{sub}. The surface morphology of ZnSe thin films studied from scanning electron microscope (SEM) showed increasing grain growth in films deposited at higher substrate temperatures.

Possibly recrystallization through diffusion in the disordered regions of the films occurred during the deposition of ZnSe at increasing substrate temperatures and correspondingly microstructural parameters of the ZnSe thin films changed abruptly. But at still higher substrate temperatures, re-evaporation of the constituent elements and molecules occurred from the ZnSe film surface. When there was a balance between the two opposite processes, microstructural parameters changed more slowly.

All the films were highly transparent (T above 70%) in the region 600–900 nm. With films deposited at higher substrate temperature, the transmission curve dropped more abruptly at the fundamental absorption edge (FAE). The high value of absorption coefficient α below the FAE were found for all the films.

Assuming slightly absorbing film on transparent substrate, the refractive index (n) and extinction coefficient (k) of ZnSe thin films were determined applying envelop method to the transmission spectrum below FAE. The optical constants of the ZnSe films were determined drawing T_{max} and T_{min} envelopes through maxima and minima positions of transmission curves taking them as continuous functions of wavelength λ through $n(\lambda)$ and $\alpha(\lambda)$. The variation of refractive index n with wavelength in the region 540–900 nm for the ZnSe films deposited at different substrate temperatures followed similar dispersion behaviour as observed by other workers. The films deposited at lower temperature (300 K and 373 K) had lower (by 6–12%) refractive index than that of bulk ZnSe, whereas those deposited at higher temperature had n values comparable with the bulk values.

We determined the absorption coefficient near the FAE of ZnSe thin film from $T\%$ and ABS values at normal incidence. The optical losses due to the effect of volume and surface imperfections were taken care of by background absorption (BA) correction. The variation of extinction coefficient k of ZnSe films along 360–900 nm wavelength region was also studied. Below FAE the k values differed for BA uncorrected films. At higher substrate temperature (473 K and 573 K), a step in k was observed at $\lambda = 400\,\text{nm}$ (photon energy, $\text{h}\nu = 3.1\,\text{eV}$). This could be ascribed to transitions from the second valance level caused by spin-orbit splitting.

The band edge behaviour was analysed assuming direct transition at the FAE. A plot of $(\alpha h\nu)^2$ against the photon energy for the films was drawn and extrapolation of the linear portion of the curves upto abscissa gave the value of band gap E_g^d for films deposited at different substrate temperature. It was observed that for room temperature deposited films the band gap value was smaller than the bulk value whereas for films deposited at higher substrate temperature, the band gap values approached the bulk value.

The results showed that the films became more stoichiometric at higher substrate temperature, grain size increased and microstrain and dislocation density decreased—reducing optical inhomogeneity and concentration of defects. This was reflected in the values of band gap, refractive index, extinction coefficient and spin-orbit splitting energy of ZnSe films deposited at higher substrate temperature, which approached the standard bulk value for ZnSe.

The I–V plots of the ZnSe films showed a linear behaviour upto a voltage of 75 volts. This showed silver paste provided ohmic contact to the ZnSe thin films. All the ZnSe films deposited at different substrate temperatures were of low conductivity of the order of $10^{-8}\,\Omega^{-1}$ cm^{-1} around room temperature. The film conductivity was found to be of n-type as determined from Seebeck effect experiment. The electrical conductivity of ZnSe films deposited at different substrate temperature was measured in the temperature range 275–325 K. The plot of $\ln \sigma$ *vs.* $1000/T$ in this temperature range was linear following the Arrhenius behaviour. However the conductivity and the activation energy did not vary visibly with increase in grain size and decrease in lattice defects and were also independent of variation in composition.

The mean free path of electron scattering (λ) in the crystallites of n-type ZnSe thin films was determined and found to be less than grain size (D) in all ZnSe films deposited at different substrate temperatures. So there exists a grain 'resistance' which can be expressed in terms of bulk mobility and hence the simple composite medium model or two-phase geometrical model is valid to explain the transport properties in these evaporated ZnSe thin films.

The electrical properties in polycrystalline semiconductor films are usually dominated by charge carriers trapped at grain boundaries. Following the two-phase model, we can express conductivity activation energy for n-type thin films as the sum of the carrier activation energy and the potential barrier activation energy. Evaporated ZnSe thin films deposited in our laboratory had very low conductivity with large thermal activation energy which indicates that carrier concentration was much lower compared to bulk impurity level (unintentional donors) as a result of total depletion of grains. Lattice defects and trace impurities were cited as deep acceptors in polycrystalline ZnSe films. So our results for evaporated ZnSe thin films can be explained by a model of fully depleted grains where carrier activation energy was greater than mobility activation energy. This occurs when dopant density in the crystallite is low so that magnitude of trap state density is greater than the product of impurity density and grain size and also the magnitude of grain size is greater than Debye length.