CHAPTER SEVEN

CONCLUSION AND SUGGESTIONS FOR FURTHER WORK

The optical and electrical characteristics of e-beam evaporated ZnS$_x$Se$_{1-x}$ thin films have been investigated in this work. The important findings in this work can be highlighted in the following manner:

(1) The structure of the film as investigated by using energy dispersion x-ray analyzer (EDX), scanning electron microscope (SEM) and x-ray diffraction (XRD), suggests that electron beam evaporation is a suitable technique to prepare ternary alloys of ZnS$_x$Se$_{1-x}$ materials from well mixed powders of ZnS and ZnSe. Depending on the initial amounts of ZnS and ZnSe in the source material, samples with sulphur compositional fraction ($x$) between 0.12 and 1.0 have been deposited onto glass substrates. The EDX analysis has shown a deviation from stoichiometric with 40% atomic percentage of ZnS in the films compositions. According to the SEM micrographs, the surfaces of the films exhibit fine-grainy morphologies with relatively large grains embedded in a matrix of finer grains. The results of XRD indicate that the films are polycrystalline with cubic structures grown along a preferential $< 111 >$ axis. The broadening of a pronounced diffraction peak along the $< 111 >$ axis has been used to estimate the grain diameter which is found to be in the range of 15.8 - 66.2 nm. Most of the samples studied in this work are subjected to a tensile stress while six of them are under a compressive stress. The compressive stress developed inside the films could be attributed to the lattice distortion produced by the
energetic particles striking the condensing film. The tensile stress could be produced by the grain-boundary relaxation effect. The cubic lattice parameter $a_0$ has been found to vary linearly with $x$ satisfying the so-called Vegard’s law.

(2) A new analytical method was proposed to estimate the thickness and the optical parameters of the films by using the experimental data of the transmission spectrum. The results obtained using this method were found to be in good agreement with the results obtained by using the well-known “envelope” method. The advantage of the proposed method stems from the non-necessity of the presence of extrema values in the transmission spectrum in order to determine the optical parameters of thin film. And a minimum of two interference fringes in the transmission spectrum is adequate to estimate the thickness of the film.

(3) The optical transmission spectra of the samples have shown high transparency in the wavelength region of 700-3200 nm. The real and imaginary parts of the refractive index and the dielectric function have been found to increase drastically with incident photon energy as the fundamental optical absorption edge is approached for each sample. The empirical relations in the dielectric theory were used to estimate the characteristic energies such as Penn energy gap, plasma energy, Fermi energy, the average energy of the valence electrons, the energy of the effective dispersion oscillator and the dispersion energy. These characteristic parameters were found to vary with the film composition. These parameters are useful in describing both the crystal structure and ionicity of solids through their influence in the refractive index behaviour.

The absorption edge can be divided into three distinct regions, the high-absorption region ($\alpha > 10^4 \text{ cm}^{-1}$), the exponential part and the weak-absorption tail. It has been found that $\alpha$ shifted towards higher energy as the concentration of sulphur $x$
increased in the film. This shift is attributed to the widening of the energy gap by increasing the amount of sulphur in the film composition. The value of $E_g$ increases from 2.58 to 3.73 eV as the value increases from 0.12 to 1.0. The variation of $E_g$ with $x$ has been found to be in a reasonable agreement with the results reported by other workers. The shift of the energy gap produced by the uniaxial stress and the grain size effect has been estimated and hence the energy gap of the corresponding free-stress single crystal materials has been deduced. The variation of $E_g$ with the grain size has been found to be in good agreement with the theoretical expressions. This made the estimation of the reduced effective mass possible. The tail in the absorption coefficient close to the band edge, which is associated with phonon-assisted transitions, was used to determine the optical phonon energies.

(4) The ohmic behaviour of the current-voltage (I-V) characteristics, that has been observed for most of the samples in the entire range of temperature concerned, suggests that a good contact has been produced between the metal electrodes and the surface of the samples. It also indicates that the number of the thermally generated free carriers exceeds the density of the injected charge carriers from the electrode. The non-ohmic behaviour observed in the (I-V) characteristics of some samples at high temperatures has been attributed to the Poole-Frenkel effect with the assumption that both donors and acceptors are present in the sample. The dc-conductivity has shown a negligible variation with temperature below room temperature followed by a gradual increase above room temperature. The model proposed by Mott and Davis has been used to estimate the activation energies in the entire range of measurements. Above 400 K, depending on the $x$ value, the activation energy of $\text{ZnS}_x\text{Se}_{1-x}$ that is required to excite the charge carriers beyond the mobility edges into the extended states has been found to be in the range of 0.54 - 0.76. However, in the temperature range of 350 -
400 K, the activation energy required for carrier excitation into the localized states at the band edges has been found to be in the range of 0.18 - 0.39 eV. Below 350 K, the activation energy has been found to be less than 0.15 eV. In this low range of temperature the conduction was assumed to be due to carriers hopping between localized states near the Fermi energy level. As the temperature was lowered, carriers were expected to tunnel to more distant sites. In this case, the conductivity was expected to follow the relation for the so-called variable-range hopping. The effect of the film structure on the dc-conductivity was demonstrated. However, it is believed that, as in all II-VI compounds with wide energy gaps, the impurities and native defects, which might be introduced unintentionally into the samples during their preparation, have a significant contribution to the conductivity.

For further work, some suggestions that might be proposed are:

(a) The effect of substrate temperature during the deposition process and the substrate materials on the properties of e-beam evaporated ZnS$_x$Se$_{1-x}$ materials might be a significant work since it is expected that the substrate temperature has a significant influence on the film structure.

(b) The estimation of the film thickness and the optical parameters could be obtained more accurately if the measured spectrum of both transmission and reflection were used in the proposed analytical method.

(c) For intensive investigation of the quantum size effect on the properties of ZnS$_x$Se$_{1-x}$ films, samples with grain size less than 150 Å are required. This can be achieved by controlling the ambient conditions during the deposition process such as the substrate temperature, or by a post-deposition treatment to the sample such as sample annealing.
(d) Since the energy gap has been found to vary with the film composition of the samples prepared by e-beam evaporation, it is believed that this technique can be employed to fabricate samples to be tested for photoelectric devices, such as LED's.

(e) For intensive study of the electrical properties of ZnS_xSe_1-x, ac-conductivity and Hall effect measurements can contribute to deep understanding on the electrical conduction mechanism in these materials.