CHAPTER 7
SUMMARY AND CONCLUSIONS

The major objective of the present work is to investigate the suitability the binary semiconductors, ZnSe, ZnTe and the quasi binary semiconductor ZnSe\(_x\)Te\(_{1-x}\) for thin film solar cells. Successful deposition of ZnSe and ZnSe\(_x\)Te\(_{1-x}\) layers was achieved using pulse plating electrodeposition method. This low cost deposition technique has good potential to be scaled up for commercial applications. Pulse plating method has produced coatings in which a systematic growth in grain size with increasing duty cycle was found. The salient features of this investigation are: The pulse plating technique has been employed for the first time to deposit ZnSe\(_x\)Te\(_{1-x}\) films. Single phase cubic ZnSe\(_x\)Te\(_{1-x}\) films have been obtained. This is the first report on photoelectrochemical cell studies. This is also the first report on AC photoconductivity studies.

In striking outcome of the results obtained on ZnSe, ZnTe and ZnSe\(_x\)Te\(_{1-x}\) films are presented in the following sections.

7.1 RESULTS ON ZnSe FILMS

ZnSe films have been deposited by the pulse plating technique at different duty cycles. This method is an easily reproducible one and is economically viable and can be scaled up for the deposition of large area films. X-ray diffractograms of the films are of single phase with cubic structure. EDAX studies indicated that the films deposited at low duty cycles had a selenium rich composition
(Zn: 48.1% and Se: 51.9%), as the duty cycle increased the composition changed to zinc side. For the films deposited at 50% duty cycle, the composition was Zn: 51.0%, Se: 49.0%. XPS spectrum exhibit the binding energies of the Zn(2p\(_{3/2}\)) and Se(3d\(_{5/2}\) and 3d\(_{3/2}\)) level. From optical absorption measurements, the band gap in the range 2.72 eV – 3.00 eV are observed for the films deposited at different duty cycles. Room temperature resistivity of the films was in the range 40–20 ohm cm for the films deposited at different deposition temperatures. Room temperature mobility of the films was in the range 20 cm\(^2\)V\(^{-1}\)s\(^{-1}\) to 8 cm\(^2\)V\(^{-1}\)s\(^{-1}\) as the duty cycle increases. Carrier density was in the range 7.81 x 10\(^{15}\)cm\(^{-3}\) to 3.90 x 10\(^{16}\)cm\(^{-3}\) as the duty cycle is increased. The films exhibited photoconductive response.

From AFM studies, the grain size is observed to increase from about 15 nm to 35 nm as the duty cycle increased from 6 to 50%. The surface roughness also increased to 0.67 nm for the films deposited at higher duty cycles.

Photoelectrochemical cell studies have indicated a higher output parameters compared to earlier reports. Ideality factor of 2.05 and a reverse saturation current density of 2.5 x 10\(^{7}\)A cm\(^{-2}\) have been obtained. Mott-schottky plots indicated n-type behaviour with a flat band potential of – 0.8 V (SCE). The slope of the line indicates an donor carrier density of 2.0 x 10\(^{16}\)cm\(^{-3}\). Spectral response measurements indicate the maximum photocurrent at 460 nm corresponding to the band gap of 2.69 eV for the films deposited at 50% duty cycle. This value matches well with the band gap value of 2.72 eV estimated from optical absorption measurements. Laser Raman studies indicated an intense peak at 252 cm\(^{-1}\) that can be attributed to the longitudinal
optical (LO) phonon mode of ZnSe. All the samples showed a single peak in the PL spectra. The peak shifts to blue region with decrease of duty cycle.

7.2 RESULTS ON ZnTe FILMS

ZnTe films were pulse electrodeposited at different duty cycles. The process is also economically viable. X-ray diffractograms of the films are of single phase with cubic structure. EDAX studies indicated that the composition of the films change from 49.5 % Zn and 50.5 % Te to 48.5 % Zn and 51.5 % Te with increase of duty cycle. Hot probe measurements indicated the films to be n-type.

The XPS spectrum exhibits the binding energies of the Zn(2p3/2) and Te(3d5/2 and 3d3/2) level. From optical absorption measurements a band gap of 2.245–2.25 eV are observed for the films deposited at different duty cycles. Room temperature resistivity of the films varied in the range of 20 to 5 ohm cm for the films deposited at different duty cycles. Room temperature mobility of ZnTe films decreases from 24 cm² V⁻¹ s⁻¹ to 10 cm² V⁻¹ s⁻¹ as the duty cycle increases. Carrier density is found to vary from 1.30 x 10¹⁶ cm⁻³ to 1.25 x 10¹⁷ cm⁻³ as the duty cycle is increased.

AFM studies indicated that the rms value of surface roughness and grain size increase from 1.5 nm to 2.4 nm and 10 nm to 50 nm respectively with increase of duty cycle from 6 % to 50 %. The films exhibit photoconductivity. Photoelectrochemical cell studies indicate a higher output parameters compared to earlier reports. Ideality factor of 1.80 and a reverse saturation current density of
2.5 x 10^7 A cm^-2 were obtained. Mott-schottky plots indicate n-type behaviour with a flat band potential of the order of 0.70 V (SCE).

Spectral response measurements indicated that the value of J_{\text{ph max}} at 525 nm corresponding to the band gap of 2.38 eV. This value matches well with the band gap value of 2.39 eV estimated from optical absorption measurements. The observed Raman peaks at about 206.8 cm^{-1} - 207.0 cm^{-1} and 411.1 cm^{-1} - 412.1 cm^{-1} are assigned to the first order and second order ZnTe LO phonon scattering respectively. The room temperature photoluminescence peak at 485.6 nm may be due to the recombination of excitons bound to neutral shallow acceptors. The peak position at 531.7 nm corresponds to a band gap value of 2.33 eV which is very close to the value of 2.33 eV for the nanocrystalline ZnTe film.

### 7.3 RESULTS ON ZnSe_{x}Te_{1-x} FILMS

Zinc selenotelluride films have been deposited for the first time by the pulse technique. This method is an easily reproducible one and is economically viable. X-ray diffractograms of the films exhibit cubic structure. EDAX studies indicated the composition to be almost equal to the composition of the precursors taken for the growth of films. XPS studies indicated the presence of Zn, Se and Te in the ratio of the starting composition. Depth profiling indicated the compositional accuracy of the films grown. Optical absorption measurements indicated the band gap to vary from 2.35 to 2.69 eV as the mole fraction is increased from 0 to 1. Band gap of the films deposited on low temperature substrates are also reported. The refractive index increased with increase of Te concentration. Electrical resistivity was found to vary from 6.0 ohm cm to 16.0 ohm cm as the ZnSe concentration increases from 0 to 1.
Mobility of the films was found to increase, 8.24 cm²V⁻¹s⁻¹ - 9.65 cm²V⁻¹s⁻¹ with increase of ZnSe concentration. Carrier concentration decreases from 1.5 x 10¹⁷ cm⁻³ to 4.5 x 10¹⁶ cm⁻³ with the ZnSe content.

AFM studies indicated that the grain size increases from 15 to 40 nm as the value of x increases from 0.1 to 0.9. The surface roughness is found to slowly increase from 0.880 to 4.235nm as the value of `x` increases from 0.1 to 0.9.

AC Photoconductivity studies were made for the first time. The films exhibit photoconductivity. Photoelectrochemical cell studies were made for the first time. Ideality factor of 1.85 and reverse saturation current density of 2.0 x 10⁻⁶ Acm⁻² were obtained. Mott-Schottky plots indicated n-type behaviour with a flat band potential in the range ~0.85 to ~0.54 V (SCE) as the mole % of ZnSe increases. Spectral response measurements indicated maximum of the photocurrent density values at different wavelengths depending upon the composition and these wavelength values correspond with the band gap values obtained from optical studies.

It is concluded that the ZnSeₓTeX₁₋ₓ films deposited by the pulse plating technique exhibit nanocrystallinity. The films prepared in this investigation possess a lot of potentialities for practical applications since the process of film preparation can be scaled for the production of large area films. Moreover, the deposition procedure can be modified to obtain nanocrystalline films of still smaller size which can be used for the production of coloured as well as white LED’s. These films can also be used in heterojunction photovoltaic devices.
7.4 PROSPECTS OF THE PRESENT WORK FOR FURTHER STUDIES

We have investigated the behaviour of ZnSe, ZnTe and ZnSeTe nano thin films and reported their growth mechanism. In efficient solar cell architecture, antireflection coatings (ARCs) play a major role in enhancing the efficiency of the solar cells by increasing light coupling into the active region of the device. A promising approach is to use textured surfaces that trap light, leading to a broadband suppression in reflection. On lithographically patterned Si photovoltaic devices, various groups have fabricated surface textured ARCs by anisotropic etching, etching through patterned masks, or via other techniques that generate porosity and/or roughness. The compound semiconductors have been intensively investigated for photovoltaic applications, including dye-sensitized solar cell (DSSC), quantum dot-sensitized solar cell (QDSSC) and core/shell nanowire solar cells. Compared with DSSC or QDSSC, core/shell nanowire solar cells have the advantages in light absorption, current transportation and charge separation. Therefore, core/shell nanostructures have been receiving increasing research attention. This promise has motivated us to fabricate noble textured Zn based nanostructures which are suitable for low-cost, large-area, photovoltaic devices and other antireflection applications in future.