CHAPTER 7

SUMMARY AND CONCLUSIONS

The salient features of this investigation are:

i) The pulse plating technique has been employed for the first time to deposit copper gallium sulphide and copper indium gallium sulphide films.

ii) Single phase chalcopyrite CuIn\(_{1-x}\) Ga\(_x\)S\(_2\) films have been obtained.

iii) This is the first report on photoelectrochemical cell studies with a pulse plated CuGaS\(_2\) and CuIn\(_{1-x}\) Ga\(_x\)S\(_2\) films.

iv) This is also the first report on Mott-Schottky studies and spectral response measurements of pulse plated CuGaS\(_2\) and CuIn\(_{1-x}\) Ga\(_x\)S\(_2\) films.

In the following, summary of the results obtained on CuInS\(_2\), CuGaS\(_2\) and CuIn\(_{1-x}\) Ga\(_x\)S\(_2\) films are presented.

7.1 RESULTS ON CuInS\(_2\) FILMS

- CuInS\(_2\) 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 in a single phase with chalcopyrite structure.

• Optical absorption measurements indicate a band in the range of 1.39 eV –1.53 eV from a plot of (αhν)^2 versus photon energy for the CuInS_2 films deposited at different duty cycles.

• The photoluminescence spectrum measurements indicated a single peak at 0.94eV.

• Laser Raman studies indicated a strong peak at 295cm\(^{-1}\) and two peaks at 240cm\(^{-1}\) and 340cm\(^{-1}\).

• The CuInS_2 films exhibited photoconductive response.

• Spectral response measurements indicated that the value of \((J_{ph})_{max}\) occurs at a wavelength value corresponding to the band gap 1.52eV. This value is nearly equal to the band gap obtained from optical measurements.

• EDAX measurements indicated that the Cu/In ratio decreased from 1.09 to 1.00 as the duty cycle increased from 6% to 50%.

• XPS spectrum exhibit the binding energies of Cu – 2p\(_{3/2}\) and Cu -2p\(_{1/2}\), In- 3d\(_{3/2}\), In -3d\(_{5/2}\) and S-2p peaks.

• The rms value of the surface roughness increased from 0.85nm to 2.5 nm with different duty cycle.
The resistivity of the CuInS\textsubscript{2} films was in the range 0.10ohmcm to 3.67ohmcm as the duty cycle is increased.

The mobility of the CuInS\textsubscript{2} films was in the range 15.54cm\textsuperscript{2} V\textsuperscript{-1}s\textsuperscript{-1} to 2.45cm\textsuperscript{2} V\textsuperscript{-1}s\textsuperscript{-1} as the duty cycle increases.

Carrier density was in the range 39.98 x 10\textsuperscript{17} cm\textsuperscript{-3} to 6.95 x 10\textsuperscript{17} cm\textsuperscript{-3} as the duty cycle is increased.

Mott Schottky plots indicate \( V_{fb} \) of 0.70V versus SCE. The value of \( N_A \) estimated from the slope of the plots yield value of 2.0 x 10\textsuperscript{17}cm\textsuperscript{-3}. The CuInS\textsubscript{2} films were p-type semiconductor.

Ideality factor of CuInS\textsubscript{2} films is 1.85 and the reverse saturation current density, \( J_0 \), was 5.1 x 10\textsuperscript{-7}Acm\textsuperscript{-2}.

Photoelectrochemical cell studies have indicated higher output parameters compared to earlier reports.

\textbf{7.2 RESULTS ON CuGaS\textsubscript{2} FILMS}

CuGaS\textsubscript{2} 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 in a single phase with chalcopyrite structure.

The band gap of the CuGaS\textsubscript{2} film was 2.30eV to 2.36eV with decrease of duty cycle.
• The Photoluminescence spectra exhibit a single peak, which shifts from 593nm to 613nm as the duty cycle decreased.

• Laser Raman studies indicated a strong peak at 308cm\(^{-1}\) which may be assigned to the A1 mode.

• The CuGaS\(_2\) films exhibit photoactivity.

• Spectral response measurements indicated that the value of \((I_{ph})_{max}\) occurs at a wavelength value corresponding to the band gap 2.29eV. This value is nearly equal to the band gap obtained from optical measurements.

• EDAX measurements indicated that the Cu/Ga ratio decreased from 1.10 to 0.99 as the duty cycle increased from 6% to 50%.

• XPS spectrum exhibit the binding energies of Cu – 2p, Ga 2p and S-2p peaks.

• The surface roughness decrease from 0.8nm to 1.2nm as the duty cycle increases.

• The resistivity of the CuGaS\(_2\) films varied from 2.10ohm cm to 15.6ohm cm with increase of duty cycle.

• The mobility of the CuGaS\(_2\) films increases from 11cm\(^2\) V\(^{-1}\)s\(^{-1}\) to 3.2cm\(^2\) V\(^{-1}\)s\(^{-1}\) as the duty cycle increases.

• The carrier concentration decreases from 2.70 \(x\) \(10^{17}\) cm\(^{-3}\) to 1.25 \(x\) \(10^{17}\) cm\(^{-3}\) as the duty cycle is increased.
• Mott-Schottky plots indicate $V_{fb}$ values, in the range 0.70V (SCE). The value of $N_D$ estimated from the slope of the plots yield value of $2.0 \times 10^{17}$ cm$^{-3}$. The CuGaS$_2$ films were p-type semiconductor.

• Ideality factor of CuGaS$_2$ films is 2.10 and the reverse saturation current density, $I_o$, was $9.1 \times 10^{-8}$ Acm$^{-2}$.

• Photoelectrochemical cell studies have indicated photo output.

7.3 RESULTS ON CuIn$_{1-x}$Ga$_x$S$_2$ FILMS

• CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition have been deposited by the pulse plating technique at 50 % duty cycle. 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 CuIn$_{1-x}$Ga$_x$S$_2$ films indicate single phase chalcopyrite structure. The lattice parameters decrease with the increase of gallium concentration.

• The band gap of the CuIn$_{1-x}$Ga$_x$S$_2$ films increased from 1.60eV to 2.275eV as the gallium concentration increased.

• The photoluminescence of the CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition indicated a broad peak at 820nm and another peak at 540nm. These correspond to the excitonic emission of CuInS$_2$ and CuGaS$_2$. While, the intensity of the peak at 540nm
increases, the intensity of the peak at 820nm decreases with increase of gallium concentration.

- Laser Raman studies indicated peaks at 293cm⁻¹ and 303cm⁻¹. As the gallium concentration increased, the peak at 303cm⁻¹ increases in intensity, and the peak at 293cm⁻¹ decreases.

- The CuInₓGaₓS₂ films exhibit photoconductive response.

- Spectral response measurements indicated that The value of (J_ph)ₘₐₓ occurs at a wavelength value corresponding to the band gap corresponding to that composition. This value is nearly equal to the band gap obtained from optical measurements.

- The peaks corresponding to Cu, In, Ga and S are observed in all cases in the EDAX spectra.

- XPS spectrum exhibit the binding energies of Cu- 2p, In-3d₅/₂, In – 3d₃/₂; Ga- 2p and S-2p peaks.

- The grain size increases as the gallium content increases and the rms value of surface roughness increases from 0.25nm to 2.2nm with an increase of gallium content.

- The resistivity increased from 14.74ohm cm to 4.52ohm cm with the decrease of gallium content.

- The mobility decreases from 3.10cm² V⁻¹s⁻¹ to 2.49cm² V⁻¹s⁻¹ as the gallium content decreases.
The carrier concentration decreased from $1.36 \times 10^{17} \text{cm}^{-3}$ to $5.54 \times 10^{17} \text{cm}^{-3}$ as the gallium content decreased.

Mott-Schottky plots of the CuIn$_{1-x}$Ga$_x$S$_2$ films of different compositions indicates p-type behaviour. Extrapolation of the plots to the voltage axis yields flat band potentials, $V_{fb}$ values, in the range 0.76 V to 0.94V (SCE) as the gallium concentration increased. The value of $N_A$ estimated from the slope of the plots yield value in the range of $1.20 \times 10^{17} \text{cm}^{-3}$ to $6.5 \times 10^{16} \text{cm}^{-3}$.

Ideality factor calculated from the slope of the straight line was 2.05. The reverse saturation current density, $J_0$, was $1.15 \times 10^{-7} \text{Acm}^{-2}$.

Photoelectrochemical cell studies were made for the first time using polysulphide redox electrolyte, since cadmium chalogenides like CdS and CdSe are stable in this electrolyte. CuIn$_{0.7}$Ga$_{0.3}$S$_2$ exhibited maximum photo output.

It is concluded that the CuIn$_{1-x}$Ga$_x$S$_2$ films deposited by the pulse plating technique exhibit nanocrystallinity. The films prepared in this investigation possess a lot of potentialities for practical applications for the process of film preparation can be scaled for the production of large area films.