CHAPTER VI
HALL EFFECT STUDIES

6.1 Introduction

One of the most important characterization technique of semiconductors is Hall effect studies. It is a simple but powerful technique for studying the transport properties. Hall effect studies are useful in the interpretation of electronic phenomenon in chalcogenide thin films. Hall effect studies along with the conductivity studies help to obtain the complete knowledge and understanding about the electrical properties of semiconducting films [1-5].

Electrical properties of bilayers of CdS and CuInSe$_2$ films prepared by vacuum evaporation in the CdS/CuInSe$_2$ solar cells have been studied by Noufi and Dick[6] and it has been compared with those of individual layers. CuInSe$_2$ films were p-type with a carrier concentration of the order of $10^{14}$ cm$^{-3}$.

Hachiuma et al[7] have prepared CuInSe$_2$ films by vacuum evaporation method with rf plasma. The film prepared at rf power 400 W
was found to have high Hall mobility $48.3 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$ because of its high crystallinity and the film was observed to be n-type with a carrier density $6.41 \times 10^{16} \, \text{cm}^3$.

Padam et al\[8\] have reported that the p-type nature of CuInSe$_2$ films got enhanced with an increase in Cu : In ratio and air annealing. They observed a reverse of this process when heated in vacuum. Near-stoichiometric or slightly indium rich CuInSe$_2$ films have been deposited by Rockett et al\[9\] using reactive magnetron sputtering. The films were of n-type or intrinsic with electron mobilities in the range $10$–$25 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$. Isomura et al\[10\] have deposited CuInSe$_2$ films by vacuum evaporation and the mobility and carrier concentration were estimated for n-type and p-type films as $2.8$ and $1.4 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$ and $3 \times 10^{19}$ and $8.9 \times 10^{20} \, \text{cm}^3$ respectively.

Castaneda and Rueda[11] have deposited CuInSe$_2$ films by both flash evaporation and electron beam evaporation techniques. They have related the n-type nature of the film to the composition with excess of electronic charge contributed by the copper and indium atoms related to the selenium double electronic acceptance. The films deposited by flash evaporation had a carrier density of $10^{17}$ holes/cm$^3$ and mobility $10$ - $100 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$ in
accordance to their copper rich composition. The electron beam evaporated films had a concentration of the order of $10^{16}-10^{17}$ cm$^{-3}$ and mobility 25 - 200 cm$^2$ V$^{-1}$ s$^{-1}$.

Terauchi et al[12] have prepared single-phase chalcopyrite CuInSe$_2$ films by selenizing the near stoichiometric Cu-In-O film prepared by r.f. magnetron sputtering. The deposited films have been found to be p-type with high conductivity. Bulk CuInSe$_2$ has been prepared by Austain et al[13] using the zone melting technique. The carrier concentration was found to be less than $10^{16}$ cm$^{-3}$ for n-type samples. The electron and hole mobility have been estimated as $\mu_e = 300$ and $\mu_h = 26$ cm$^2$ V$^{-1}$ s$^{-1}$ respectively.

CuInSe$_2$ single crystals have been grown from melt by Migliorato et al[14]. They have reported that crystals grown from melts containing a slight selenium excess or annealed under maximum selenium pressure as p-type and crystals grown from excess indium melts or annealed under minimum selenium pressure as n-type. The p-type crystals have been found to have a carrier concentration of the order of $10^{18}$ cm$^{-3}$ and mobility
10 cm$^2$ V$^{-1}$ s$^{-1}$ and that of n type crystals are of the order of $10^{17}$ cm$^{-3}$ and 250 cm$^2$ V$^{-1}$ s$^{-1}$ respectively.

The dependence of magnitude and type of conductivity in CuInSe$_2$ thin films on composition has been discussed by several workers\cite{15-17}. Nishitani et al\cite{15} have reported that copper rich films are p-type and indium rich films are n-type. However Noufi et al\cite{16} and Yamanaka et al\cite{17} have reported that there existed a p-type conduction region even in the indium rich composition which indicated that copper vacancies are responsible for achieving higher conversion efficiency in n-(Zn,Cd)S/CuInSe$_2$ solar cells. Noufi et al\cite{16} have reported that the electrical behaviour of CuInSe$_2$ films depends not only on In/Cu composition ratio but also on Se/(Cu+In) ratio. They have observed that change in resistivity and conduction type in CuInSe$_2$ material can be easily achieved by changing the stoichiometry. It has been observed that p-type CuInSe$_2$ films with a single phase could be obtained only in a limited composition region called, “the v-shaped region” where the hole concentration ranged from $10^{14}$ to $10^{20}$ cm$^{-3}$ and highly conductive films could not be obtained in n-type easily.
Hall effect measurements have been carried out by Champness and Ahmad[18] on monocrystalline CuInSe₂ samples. The samples were found to be p-type with carrier concentration of $2.5 \times 10^{17}$ cm$^{-3}$ and mobility 25 - 50 cm$^2$ V$^{-1}$ s$^{-1}$. It has been reported that the conductivity of CuInSe₂ changed to n-type when annealed and exist only on the surface with the interior remaining as p-type. Tell and Shay[19] have reported that CuInSe₂ compound was p-type when annealed under maximum selenium pressure with a hole concentration of $1 \times 10^{18}$ cm$^{-3}$ and mobility $10$ cm$^2$ V$^{-1}$ s$^{-1}$. When annealed under minimum selenium pressure the compound was of n-type with carrier concentration $4 \times 10^{17}$ cm$^{-3}$ and mobility $320$ cm$^2$ V$^{-1}$ s$^{-1}$.

Tanaka et al[20] have studied the effect of Mg ion implantation on the electrical properties of CuInSe₂ films and have observed the conductivity of as grown films as n-type with a carrier concentration of $10^{15}$ cm$^{-3}$. On annealing the carrier concentration was found to decrease to the order of $10^{14}$ cm$^{-3}$. On Mg implantation the carrier concentration was observed to increase as the Mg atoms act as donors. The type of conductivity in CuInSe₂ films prepared by coevaporation of the elements using an electron bombardment heating technique has been determined using hot-probe.
method by Szot and Haneman [21]. The films exhibited p-type conductivity unless the selenium composition was in excess of 1–2 %.

The effect of sputter conditions on the electrical properties of CuInSe₂ films have been studied by Kim and Im[22]. The films deposited with sputtered molecularity M greater than 0.31 were found to be p-type and with M less than 0.28 as n-type. The mobility of charge carriers in samples with M = 0.31 and M > 0.31 was found to be 15 and 3 cm² V⁻¹ s⁻¹ respectively. CuInSe₂ films have been deposited by Kazmerski et al[23] to form a heterojunction solar cell with CdS using three-source evaporation technique. The CuInSe₂ layer in the solar cell has been reported to have a carrier concentration of 10¹⁷ cm⁻³.

Bates et al[24] have reported that CuInSe₂ film with a composition Cu : In : Se ratio in the vicinity 1 : 1 : 4 is p-type with a conductivity 0.1 Ω·cm. Niki et al[25] have deposited CuInSe₂ films by molecular beam epitaxy. The deposited films were of p-type in nature with hole concentration ≈ 10¹⁹ cm⁻³.
Kristensen et al[26] have reported that near stoichiometric CuInSe$_2$ films are always $p$-type. Films deposited at high substrate temperatures have been observed by them to be indium deficient and $p$ type and films deposited at low substrate temperature were copper deficient and $n$-type. In copper rich films indium vacancies act as acceptors resulting in $p$-type character. In copper deficient films indium content is large and indium interstitials or indium atoms on copper sites act as donors. They have reported that the films deposited at substrate temperatures above 445$^\circ$C are $p$-type and the ones deposited below are $n$-type.

Padam et al[27] have observed that $p$-type nature in CuInSe$_2$ films enhances with increase in Cu : In ratio and air annealing. But when heated in vacuum the reverse of this was observed. Fitzgerald and Potrous[28] have reported that the majority carrier type in CuInSe$_2$ films depend on substrate temperature. It has been observed that the change from $n$ to $p$-type occurred at substrate temperature in the range 170 – 190$^\circ$C. CuInSe$_2$ films have been deposited by Fray and Lloyd[29] using vacuum evaporation and have reported a carrier concentration of $2 \times 10^{20}$ cm$^{-3}$ for $p$-type films.
Kohiki et al[30] have reported that the conductivity of the as-deposited CuInSe₂ films is n-type and it can be changed from n-type to p-type by doping group five elements (N, P, Sb or Bi), which substitute for selenium. Tomlinson et al[31] have observed n-type conductivity in indium rich CuInSe₂ films and p-type conductivity in copper and selenium rich films.

Masse et al[32] have grown p-type and n-type CuInSe₂ films by close-spaced vapour transport using a vertical tube arrangement. It has been reported that the electrical conductivity of the films can be varied from n-type to p-type by a simple adjustment of source and substrate temperatures during the growth.

Garcia-Cuenca et al[33] have studied the Hall properties of CuInSe₂ films prepared by vacuum evaporation. The carrier density was found to be in the range of $10^{13}$ - $10^{19}$ cm$^{-3}$ for p-type samples and the carrier density is found to increase with an increase in Cu/In ratio. This variation of carrier density with Cu/In ratio was seen only in films in which Se/(Cu + In) ratio was around 1.0 and Cu/In ratio lower than 1.6. The p-type conductivity of the films has been attributed to the indium vacancies that act as acceptors.
and the acceptors are partially compensated by selenium vacancies that act as donors. The mobility has been reported to be lower than $3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for p-type samples.

Deb[34] has reported that for an efficient solar cell the carrier concentration should be in the range $10^{16} - 10^{17} \text{ cm}^{-3}$ and has also reported that p-type conduction can be achieved by either cation vacancies or anion interstitials. Copper to indium ratio at constant selenium concentration has been reported to be responsible for carrier type and carrier concentration. Yamaguchi et al[35] have reported that CuInSe$_2$ films with composition Cu : In : Se = 24.6 : 26.3 : 49.1 are n-type as they are indium rich.

Tanaka et al[36] have observed that the conductivity and carrier concentration in as-grown CuInSe$_2$ films as n-type and $3 \times 10^{16} \text{ cm}^{-3}$. On annealing it was found that the carrier concentration decreased to $10^{14} \text{ cm}^{-3}$. Tanaka et al[37] have reported the carrier concentration and Hall mobility of as-deposited n-type CuInSe$_2$ films as $10^{16} \text{ cm}^{-3}$ and $40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively. When the films were irradiated using 8 MeV electron beam no significant change in carrier concentration was observed for electron fluences below $3 \times 10^{16} \text{ e cm}^{-2}$ but the carrier concentration and Hall
mobility started to decrease when the electron flux exceeded $10^{17} \text{ e cm}^{-2}$.

Bindu et al[38] have reported that CuInSe$_2$ films are p-type when the Cu/In ratio is 0.9. As the ratio increases the films become more p-type and when the ratio becomes 1.3 the films exhibit degenerate p-type nature.

From the detailed literature survey it is clear that although several workers have carried out Hall effect studies on CuInSe$_2$ films the studies on CuInSe$_2$ films deposited by close-spaced vapour transport technique has been carried out only by Masse et al[32]. Considering the importance of Hall characterization in the present investigation Hall measurements have been made on CuInSe$_2$ films of different thicknesses deposited at source temperatures 713 K and 843 K. From this, the Hall coefficient, Hall mobility, carrier concentration and the type of conductivity present in the CuInSe$_2$ films deposited by close-spaced vapour transport technique have been determined and the results are discussed in detail.

6.2 Theory

Hall found that when a magnetic field is applied at right angles to the direction of current flow in a conductor a voltage is developed across the conductor in a direction perpendicular to both the current and the magnetic field. This phenomenon is known as Hall effect. In Hall effect the charge
carriers are deflected to one side of the conductor as a result of Lorentz force experienced by them. A careful analysis of the experimental data will give information regarding the nature of charge carriers and their densities. The polarity of the obtained Hall Voltage ($V_H$) can be used to determine the type of the charge carriers.

The arrangement used for Hall effect studies is shown in figure 6.1. If current $I$ is flowing in the $x$ direction and a magnetic field $B$ is applied in the $y$ direction as shown, both positive and negative charge carriers are deflected upward in the magnetic field. The Hall voltage is measured between the points A and C. If the charge carriers are positive they move with a drift velocity $V_d$ in the direction of current and if they are negative their direction of motion will be opposite to the direction of current. If $q$ is the charge of the particle the magnetic Lorentz force acting on the particle is

$$F_m = q V_d B \quad (6.1)$$

In both the cases under the action of the magnetic force the charged particle will be deflected upwards. Thus there will be an accumulation of charges on the upper side and this will set up a potential difference between
Fig. 6.1 The Hall effect study
the sides. When the charge carriers are positive the upper side of the sample will be at a higher potential when compared to the lower side. Thus by finding the sign of the Hall voltage the sign of the charge carriers in the conductor can be identified. As more and more charges get accumulated the Hall voltage increases and a Hall electric field \(E_H\) is developed. The relation between the Hall field and Hall voltage is

\[
E_H = \frac{V_H}{d} \quad (6.2)
\]

where ‘d’ is the width of the specimen. This Hall field exerts an electric force \(F_E = qE_H\) opposite to the magnetic force and at equilibrium the electric force just balances the magnetic force and therefore at equilibrium,

\[
BqV_d = qE_H
\]

\[
V_dB = E_H \quad (6.3)
\]

The drift velocity is given by

\[
V_d = \frac{I}{nqA} \quad (6.4)
\]

where ‘n’ is the carrier concentration and A is the area of cross section of the sample, which is given by

\[
A = t \times d \quad (6.5)
\]

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where 't' is the thickness of the sample.

Using equations (6.2) to (6.5) $V_H$ can be obtained as

$$V_H = \frac{I B}{n q t} \quad (6.6)$$

In the above equation the quantity $1/ nq$ is referred as Hall coefficient $R_H$

$$R_H = \frac{1}{n q} \quad (6.7)$$

The Hall coefficient can also be written using equation (6.6) as

$$R_H = \frac{V_H t}{I B} \quad (6.8)$$

The Hall mobility ($\mu_H$) defined as drift velocity per unit electric field can be determined using the relation

$$\mu_H = R_H \cdot \sigma \quad (6.9)$$

where $\sigma$ is the electrical conductivity. The carrier concentration($n$) is determined using the relation

$$n = \frac{1}{R_H \, e} \quad (6.10)$$

### 6.3 Measurement

Hall effect measurements on CuInSe$_2$ films deposited by close-spaced vapour transport technique has been carried out by Van der-Pauw method. The ohmic contacts have been made using silver paste and fine copper wires have been used for electrical connections. The CuInSe$_2$ film is kept in a
uniform magnetic field supplied by an electromagnet. A gauss meter has been used to measure the magnetic field. A d.c. power supply of 0-30 V has been used to supply a constant current in the range of 0-2 amperes. The Hall voltage has been measured using an electrometer (Keithley model 2001). The experimental arrangement is shown in figure 6.2.

6.4 Results and discussion

Hall voltage has been measured for CuInSe$_2$ films of thicknesses in the range 400 to 2600 nm deposited at source temperatures 713 K and 843 K. Positive Hall voltage has been observed for films deposited at 843 K. The observed positive Hall voltage clearly suggests that the films deposited at source temperature 843 K are of p-type nature with holes as the majority charge carriers. Films deposited at source temperature 713 K exhibited negative Hall voltage. This suggests that films deposited at source temperature 713 K are n-type with electrons as their majority charge carriers [39]. The energy dispersive x-ray analysis (EDAX) results as discussed already in chapter III also revealed that films deposited at 713 K are indium rich and those deposited at 843 K are copper rich. Thus the Hall effect study confirms that the copper rich films are p-type and indium rich films are n-type. This behaviour has been confirmed by several workers.
Fig. 6.2 Experimental arrangement to measure Hall voltage
In copper rich films indium vacancies act as acceptors producing p-type character. However as indium concentration is large in indium rich films, the indium atoms occupying interstitial sites or indium atoms on copper sites act as donors and give rise to n-type character.

From the obtained Hall voltage for different magnetic fields, the Hall coefficient has been determined for both p-type and n-type CuInSe$_2$ films. Figures 6.3 and 6.4 show the dependence of Hall coefficient on applied magnetic field for the films deposited at source temperatures 713 K and 843 K. The variation of Hall coefficient with film thickness for the films deposited at source temperatures 713 K and 843 K are shown in figures 6.5 and 6.6 respectively. The Hall coefficient is found to remain almost constant with applied magnetic field but it increases with increase in film thickness. This is in accordance with the behaviour expected for semiconductor films[40]. The observed increase in Hall coefficient with increase in film thickness can be attributed to the decrease in defect density of surface[41].

The variation of carrier concentration of n-type CuInSe$_2$ films, deposited at source temperature 713 K, with film thickness is shown in figure 6.7. The carrier concentration is found to decrease with increase in
Fig. 6.3 Plot of Hall coefficient versus magnetic field of CuInSe$_2$ films.
Fig. 6.4 Plot of Hall coefficient versus magnetic field of CuInSe$_2$ films
Fig. 6.5. Variation of Hall coefficient with thickness of CuInSe$_2$ films

$T_s = 713$ K

Hall coefficient (cm$^3$ C$^{-1}$)

Thickness (Å)

Fig. 6.5. Variation of Hall coefficient with thickness of CuInSe$_2$ films
Fig. 6.6. Variation of Hall coefficient with thickness of CuInSe$_2$ films

$T_s = 843$ K
Fig. 6.7 Thickness dependence of carrier concentration in CuInSe$_2$ films.
film thickness. The value of the carrier concentration obtained which is of the order of $10^{18}$ cm$^{-3}$ is in good agreement with the reported values of several workers for n-type films\cite{10,11,14,34}. The carrier concentration of p-type CuInSe$_2$ films, deposited at source temperature 843 K, is of the order of $10^{19}$ cm$^{-3}$ and is in agreement with that of various other workers\cite{24,26,30,34}. Figure 6.8 shows the variation of carrier concentration of p-type films with film thickness. The carrier concentration is found to decrease with increase in film thickness. As Hall coefficient is found to increase with film thickness, the carrier concentration decreases.

The variation of mobility with film thickness and magnetic field in CuInSe$_2$ films deposited at source temperature 713 K is shown in figure 6.9. The mobility is found to be nearly 5.5, 11.2 and 30 cm$^2$ V$^{-1}$ s$^{-1}$ for films of thickness 419 nm, 1411 nm and 2504 nm respectively. These values are in good agreement with the reported values of Rockett et al\cite{9}. The dependence of mobility with film thickness and magnetic field of CuInSe$_2$ films deposited at source temperature 843 K is shown in figure 6.10. The mobilities are nearly 2, 3 and 10 cm$^2$ V$^{-1}$ s$^{-1}$ for p-type films of thickness 200 nm, 598 nm and 2553 nm respectively. The values are in good agreement with the reported values\cite{10,33}. The mobility is found to exhibit
Fig. 6.8 Plot of carrier concentration versus thickness of CuInSe$_2$ films

$T_s = 843$ K
Fig. 6.9 Plot of mobility versus magnetic field of CuInSe$_2$ films

$T_s = 713$ K

- $t = 419$ nm
- $t = 1411$ nm
- $t = 2504$ nm
Fig. 6.10 Plot of mobility versus magnetic field of CuInSe$_2$ films
a small variation with magnetic field which may be due to the variation of the resistance of the material with magnetic field.
References


