



HALL PARAMETERS OF UNDOPED AND DOPED FILMS OF CuInS_2 GROWN ON GLASS SUBSTRATES BY CBD

Sumita Sengupta

Department of Physics, SSPU, Bhilai (CG)- 490020 India

Corresponding author: sumita.2006@gmail.com

Abstract

The present paper is all about measuring Hall parameters in various undoped and rare earth doped thin films of copper indium sulphide grown by using chemical bath deposition (CBD) method in alkaline medium at different temperature and different volume of dopant. The thickness of the synthesized samples was determined by using gravimetric method. The resistivity (ρ) was determined by using four probe methods. Hall voltages were measured for varying magnetic and electric fields. The value of R_H and μ_H do not depend on magnetic and electric fields, but they change with film thickness. All grown films showed P-type conductivity irrespective of thickness. The value of n_H depends on thickness of films. Observation depicts that carrier concentration decreases with increase of thickness of the film. High mobility and high conductivity have been obtained in Ho (6ml) doped film grown at 80°C .

Keywords: Hall coefficient, Mobility, Thin films, CBD

1. Introduction

CuInS_2 is one of the members of the ternary chalcopyrite compounds $\text{A}^{\text{I}}\text{B}^{\text{III}}\text{X}_2^{\text{VI}}$. Ternary semiconductor CuInS_2 is becoming current interest as it is having photovoltaic device application potential [1,2] such as in economical hetero-junction solar cells and photovoltaic detectors [3]. Also, it has perspective application in biomedical labelling[4]. The first thin film of CuInS_2 was reported by [5] using the single and double source method. Since then many researchers have synthesized CuInS_2 thin films by various methods such as chemical vapor deposition [6], three sources molecular beam epitaxy [7], electro deposition [8], spray pyrolysis [9], co

evaporation [10], SILAR [11], reactive sputtering [12], ion layer gas reaction [13], CVD [14]& chemical bath deposition [15-18]. Hall measurement is the significant technique to get the concentration of charge carrier, mobility and resistivity of a sample which is conductive. Thin films of polycrystalline or amorphous materials are useful in many modern devices. Because of low mobility and high resistance, it is challenging to perform Hall measurements on these films. Vander Pauw; 1958[19] apprehended that Hall measurements are suitable both for rectangular shaped samples and at the same time can be used for arbitrary shaped samples. The sample layer should be homogeneous, thickness should be uniform and must be free from holes. This makes sample preparation simple especially when it is for solar cell absorbers. In Zn-Te thin films, the Hall effect measurements are carried out by many researchers [20-21].

2. Experimental Method

Doped and undoped CuInS_2 films were grown on microscopic glass substrates by CBD method. Prior to use, care has been taken to clean the substrates many a times by regular detergent, acetone and deionised water. Solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1M), InCl_3 (0.1M) and thiourea has been used as precursors in appropriate proportion. Then ammonia (25%) and TEA were added. Stirring upto 10min has been provided for homogeneous deposition of films. For depositing doped films; we have added flux CdCl_2 and nitrates of rare earth samarium and Holmium to the solution. The temperature of the liquid bath was 80°C and it remains constant for all deposited films.

3. Results and Discussions

For measuring Hall mobility we have to first measure Hall potential (V_H) in the presence of

magnetic field which is at right angle direction to the current. The voltage difference will be generated which will be transverse to the current and magnetic field (B). Hall potential (V_H) can be measured across the device. The thickness of the synthesized samples was determined by using gravimetric method. The thickness of the undoped films is in the range of 108.1 μ m to 49.78 μ m whereas thickness of doped films is in nm range. The resistivity (ρ) was determined by using four probe methods. Hall coefficient R_H , charge carrier density n_H and mobility μ_H were measured using the equations:

$$R_H = \frac{V_H \cdot t}{I \cdot B} \quad \text{----(1)}$$

$$n_H = \frac{1}{R_H \cdot e} \quad \text{----(2)}$$

$$\mu_H = \sigma \cdot R_H \quad \text{----(3)}$$

Where V_H = Hall voltage, I = current, B = Magnetic field and t = thickness of film.

To elucidate the consequence of rare earth element on electrical properties such as resistivity and mobility of CuInS_2 films, Hall measurement was carried out and the results are represented in Table 1. Silver paste was used for making all the ohmic contacts. The films were kept in a uniform magnetic field which has been supplied by an electromagnet with a dc power supply. In order to measure the magnetic field strength a gauss meter has been used. In all the films whether it is doped or undoped the value of Hall coefficient (R_H) is positive thus type of charge carriers were "holes" and type of synthesized films were of p-

type. Fig.1, Fig.2 and Fig.3 shows graph between Hall voltage and current for CuInS_2 films at 60 $^\circ\text{C}$, 70 $^\circ\text{C}$ and 80 $^\circ\text{C}$. When deposition temperature is increased from 60 $^\circ\text{C}$ to 80 $^\circ\text{C}$; electrical resistivity of films decreases. The Hall mobility increases with temperature. Similar behaviour has been reported by [22] and [23]. This rise in mobility with temperature is because of $T^{3/2}$ law highlighted by [24]. Another reason is obviously caused by increase in grain size due to recrystallization processes. For film prepared at 60 $^\circ\text{C}$, grain size was 22.81nm, and it increased to 22.9 nm for film prepared at 80 $^\circ\text{C}$. In Sm doped film when volume of Sm increases then resistivity decreases. Same behaviour is observed for Ho doped CuInS_2 thin films. It was found that the mobility of charge carrier reduces with the increasing volume of doping element. The reason may be the decrease in thickness of the film with increasing volume of doping element. This behaviour may be due to the decrease of trapping centers of charge carriers with the increase of film thickness. This is because of decreased grain boundary scattering, which limits the mobility in thinner films (Sze; 2007). Hall mobility of CIS: CdCl_2 , Ho (6ml) film is higher than other doped films. The conductivity of CIS: CdCl_2 , Ho (8ml) film is high as atomic percentage of copper is high in this film confirmed from EDAX.

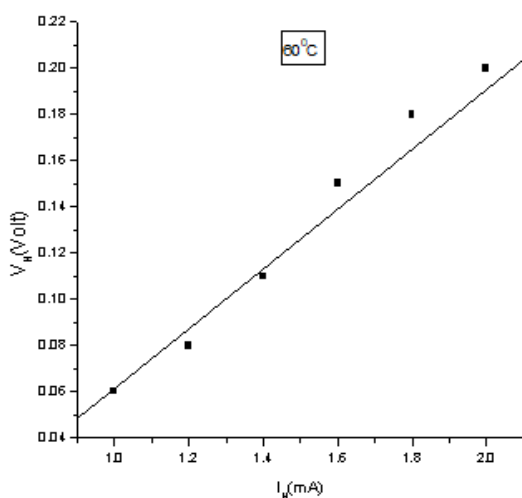


Fig1. Graph between Hall voltage and current at 60 $^\circ\text{C}$

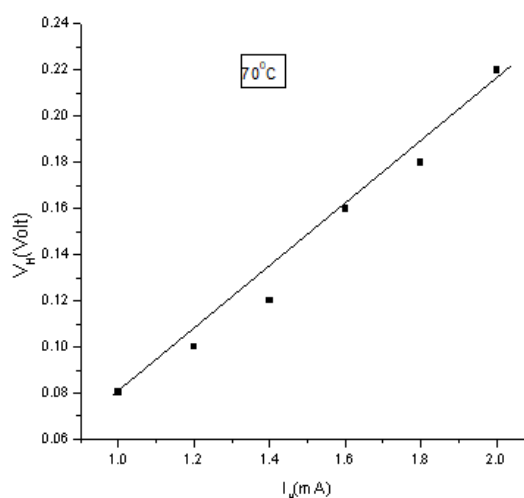


Fig2. Graph between Hall voltage and current at 70 $^\circ\text{C}$

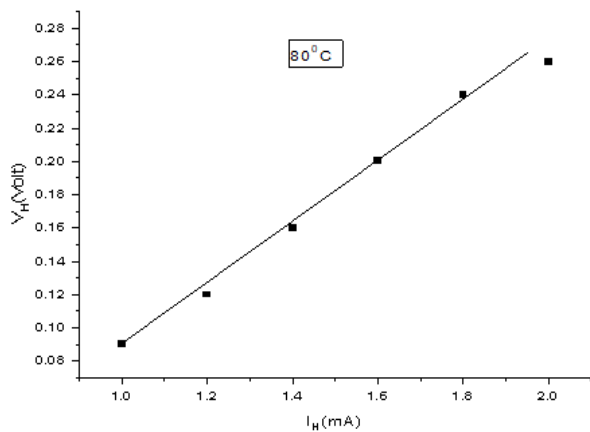


Fig3. Graph between Hall voltage and current at 80°C

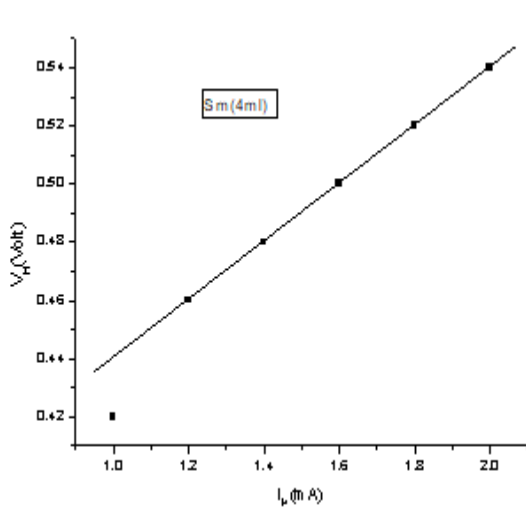


Fig4. Graph between Hall voltage and current for CIS:Sm(4ml) doped film

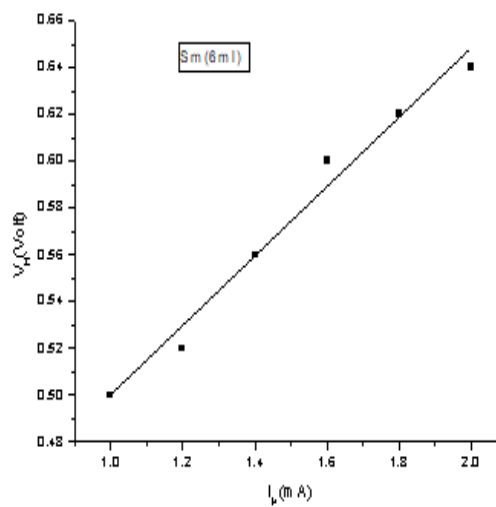


Fig5. Graph between Hall voltage and current for CIS:Sm(6ml) doped film

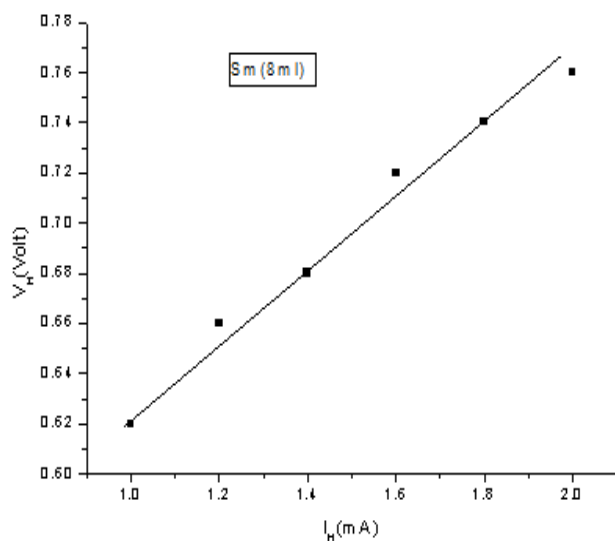


Fig 6. Graph between Hall voltage and current for CIS:Sm(8ml) doped film

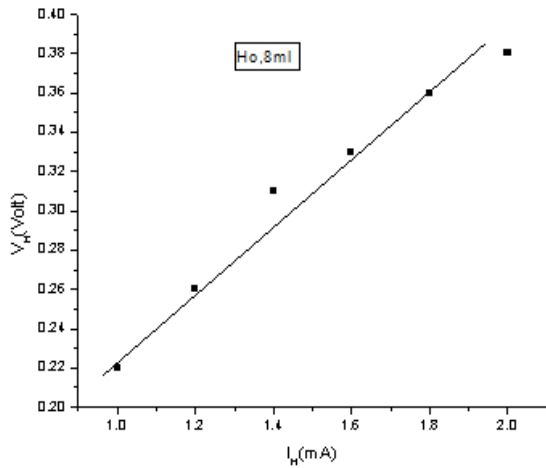


Fig. 7 Graph between Hall voltage and current for film CIS:Ho(6ml)

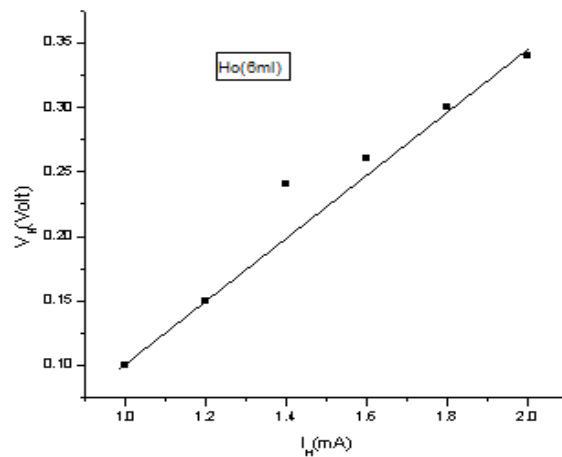


Fig. 8 Graph between Hall voltage and current for film CIS:Ho(8ml)

Table 1: Hall measurement results of various undoped and doped CuInS₂ thin films

Sample	V_H/I_H (Ω)	R_H (cm^3/c)	Type of carriers	Concentration of charge carrier [cm^{-3}]	σ at RT [$\Omega\text{-cm}^{-1}$]	Hall mobility [cm^2/Vs]	ρ [$\Omega\text{-cm}$]
CIS at 60 ⁰ C	100	103.1	Holes	6.0×10^{16}	0.012	1.25	83.3
CIS at 70 ⁰ C	175	86.97	Holes	7.0×10^{16}	0.010	0.93	100
CIS at 80 ⁰ C	140	89.74	Holes	6.9×10^{16}	0.016	1.44	62.5
CIS: CdCl ₂ , Sm (4ml)	100	79	Holes	7.9×10^{16}	0.020	1.58	50
CIS: CdCl ₂ , Sm (6ml)	150	97	Holes	6.4×10^{16}	0.015	1.50	66.6
CIS: CdCl ₂ , Sm (8ml)	150	61	Holes	1.0×10^{17}	0.025	1.56	40
CIS: CdCl ₂ , Ho (6ml)	250	128.5	Holes	4.8×10^{16}	0.019	2.51	51.2
CIS: CdCl ₂ , Ho (8ml)	100	47	Holes	1.3×10^{17}	0.031	1.50	32.2

The resistivity of CIS: CdCl₂, Sm (6ml) is very high. The conductivity of all doped films is higher than undoped film. In general, increased doping will lead to increased conductivity. The reason is higher value of carrier concentration.

4. Conclusions

At last, we can conclude that doped and undoped thin films of CuInS₂ has been obtained successfully by chemical method in a liquid bath. Hall parameters have been studied comprehensively. Hall mobility of CIS: CdCl₂, Ho (6ml) film is higher than other doped films. The conductivity of CIS:

CdCl₂, Ho (8ml) film is high as the atomic percentage of copper is high in this film. These thin films with high carrier mobility will permit developing devices that incur maximized current flow at lower power levels, with faster switching times and higher bandwidth. Hall effect measurements are decisive for the future of the electronics industry.

References

- [1]. Shay, J. L.; Wernick, J. H. 1975. Pergamon Press, Oxford. 50.
- [2]. Yu, K.; Ng, P.; Ouyang, J.; Zaman, M. B.; Abulrob, A.; Baral, T. N.; Fatehi, D.; Jakubek, Z. J.; Kingston, D.; Wu, X. 2013, *Low, ACS Applied Materials & Interfaces*, 5: 2870-2880.
- [3]. Wagner, S; Shay, J. L; Migliorato, P. H.M; Kasper. 1974, *Appl. Phys. Lett*, 25: 234.
- [4]. Nakamura, H.; Kato, W.; Uehara, M.; Nose, K.; Omata, T.; Otsuka-Yao-Matsuo, S.; Miyazaki, M.; Maeda, H. 2006, *Chemistry of Materials*, 18: 3330-3335.
- [5]. Kazmerski, L.L., Ayyagari, M. S. and Sanbom, G. A. 1975. *J. Appl. Phys.* 46:4865.
- [6]. Hollingsworth, J. A.; Banger, K. K., Jin, M. H.C.; Harris, J. D.; Cowen, J. E.; Bohannane, E.W., Switzere, J. A., Buhro, W., Hepp, A.F. 2003. *Thin solid films*. 431: 63-67.
- [7]. Muffer, H. J; Fischer, C. H; Diesner, K. 2001. *Solar Energy Material Sol. Cells*, 67: 121.
- [8]. Kuranouchi, S., and Nakazawa, T. 1998. *Solar Energy Material Solar cells*. 50:31-36.
- [9]. Zouaghi, M.C., Ben Nasrallah, T., Marsillac, S., Bernede, J. C., Belgacem, S. 2001. *Thin solid films* 382: 39- 46.
- [10]. Scheer, R., Luck, I., Kanis, M., Matsui, M., Watanabe, T., Yamamoto, T. 2001. *Thin solid films*. 392: 1-10.
- [11]. Kundakci, M. 2010. *Chinese journal of chemical physics*. 23:582.
- [12]. Watanabe, T., Nakazawa, H; Matsui, M., Ohbo, H; Nakada, T. 1997. *Solar Energy Material and solar cells*, 49: 357-363.
- [13]. Qiu, J; Jin, Z; Qian, J; Shi, Yong; Wu, W. 2005. *Journal of Crystal Growth*, 282 :421-428.
- [14]. Harris, J. D., Banger, K. K., Scheiman, D. A., Smith, M. A., Jin, M. H. C., and Hepp, A. F. 2003. *Materials Science and Engineering*: B, 98: 150-155.
- [15]. Pathan, H. M., and Lokhande, C.D. 2004. *Applied Surface Science*, 239 (1):11-18.
- [16]. Guha, P.; Das, D.; Maity, A. B.; Ganguli, D., Chaudhuri, S. 2003. *Solar Energy Material Solar cells*. 80:115-130.
- [17]. Cui, F., Wan, L., Xi, Z., Sun, Y., Yang, D. J. 2009. *Material Science Material Electron*. 20: 609 -613.
- [18]. Jindal, S; Giripunje, S.M; Kondawar, S.B; Koinkar, P. 2018, *Journal of Physics and Chemistry of Solids*, 114: 163.
- [19]. Larsen, T. L., Stevenson, D. A., *J Appl Phys*. 1973, 44, 843.
- [20]. Van-der Pauw, L. J. 1958. *Philips Technical Review*. 20:220.
- [21]. Tubota, H., Suzuki, H., Hirakawa, K., *J Phys Soc Japan*. 1960, 15, 1701.
- [22]. Soliman, L. I. 1994, *Indian journal of pure and applied physics*, 32:166.
- [23]. Abo, A. M; Zayed, H. A; Soliman, I. I. 1993, *Thin solid films*, 229(2): 232-236.
- [24]. Goswami, A. 1996. *Thin Film Fundamentals*, New Age International (P) Limited Publishers, New Delhi, 280.