STUDY OF OPTICAL, ELECTRICAL PROPERTIES OF $CuGaTe_2$ PREPARED THIN FILMS BY SPRAY PYROLYSIS

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ABSTRACT.

Spray pyrolysis is a simple and inexpensive method to prepared thin film on large area. A thin film of $CuGaTe_2$ is a promising chalcopyrite semiconducting material for solar cell fabrication. We have prepared $CuGaTe_2$ thin films on glass substrate at 350^{0}C by this method, using aqueous solution of Copper chloride, Gallium chloride and Tellurium tetra-chloride and studied their optical and electrical properties. The conductivity of the films was of p-type determined by Hot- Probe method. Resistivity of the films was measured for the temperature ranging from 77 K to 473 K by using Four Probe method. The activation energy calculated from Arrhenius Plot. The films are not doped intentionally and therefore the defects observed in intrinsic nature. In very low temperature region a variable range hopping conduction mechanism appears to be operative. Hall mobility and carrier concentration at room temperature were calculated using Van der Pauw-Hall method. The optical band gap was 1.23 eV calculated from an analysis of optical transmission spectra which were measured by UV-1800 Shimadzu Spectrophotometer. The energy band gap show direct allowed transition.

Keywords: $CuGaTe_2$, UV-1800 Spectrophotometer, Four Probe Method, etc.

1. INTRODUCTION

The ternary compound of Cu-III-VI_2, which have a chalcopyrite structure for many applications [1-4]. These compounds are also very useful in upstanding and extending the basic physical concepts of the electrical conduction mechanism involved in elemental and binary compound semiconductor. The electrical conductivity of $CuInSe_2/S_2$ down to liquid Nitrogen, temperature in both low and high. The variable range hopping conduction mechanisms have been extensively studied [5-7]. Though I-III-Se_2 compound have received much attention in recent years, there are relatively fewer studies on I-III-Te_2. Devices require materials with reproducible electrical and optical properties and as such there is currently much interest in the study of the physical properties of I-III-VI_2 compounds. $CuInTe_2$ is one such compound which is not completely investigated in thin film form [8-10]. This is because of the complex nature around $(Cu_2Te)_{0.5}$, $(Ga_2Te_3)_{0.5}$ of its pseudo-binary phase diagram that leads to the formation of high concentration of intrinsic defects which origination from the deviation of its ideal stoichiometry [11-15].

Only limited number of works on its electrical and optical properties appears in the literature. Hence in this paper we have reported more detailed information on electrical and optical properties of $CuGaTe_2$ thin films by spray pyrolysis method. The results obtained are reported and discussed. Thickness of the films was measured by Michelson Interferometer. Absorption edge analysis was carried out using transmittance verses wavelength in the range of 350 nm to 1100 nm on UV-1800 Shimadzu spectrophotometer. Electrical conductivity for the temperature range 77 K to 473 K was studied.

2. PREPARATION METHOD

Aqueous solution of Cupric Chloride, Gallium Chloride and Tellurium Tetra-chloride was prepared in double distilled water. Molarities of each solution was of 0.02 M. Chemicals were used as AR-grade. Each solution was mixed together in the proportion of 1: 1: 3.2 by volume. The films deposited have tellurium deficiency if the ratio of the solution is taken as 1:1:2. Excess Tellurium is used to remove this deficiency. The rate of flow was maintained at 3.5 ml/min. Then they spray on pre-heated glass substrate at 350^0C. Glass sprayer moved mechanically to and fro to avoid the droplet on the films and ensure instant evaporation. Schematic experimental set-up of spray pyrolysis technique as shown in fig. 1. To prepare low resistivity p- type films a slight excess of selenium, sulfur and tellurium [14-19].

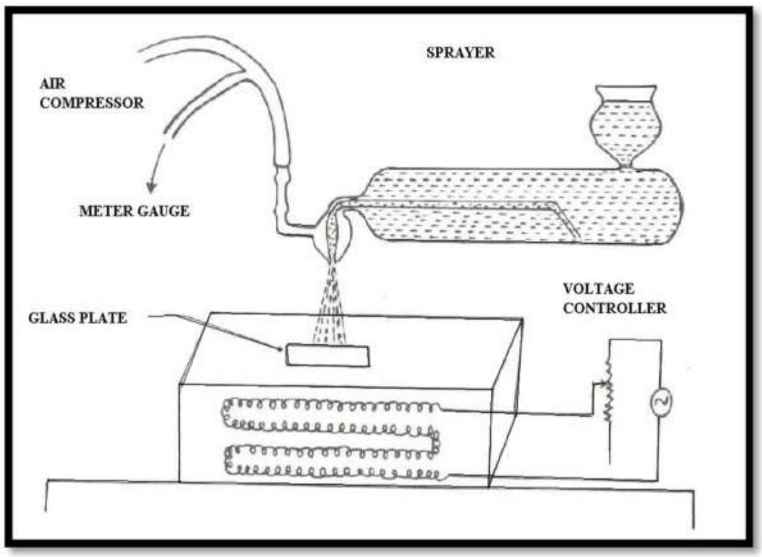

Fig. 1. Experimental set-up of Spray pyrolysis technique

3. CHARACTERZATION TECHNIQUES

3.1 OPTICAL STUDY

The optical absorption spectra are recorded from 1100 to 350 nm wavelength using SHIMADZU UV-1800 Spectrophotometer at room temperature. The relationship between absorption coefficient and optical band gap is expressed to calculate the band gap of the compounds by the following relationship,

$$\alpha = 1/t \log (I_o/I)$$

The variation of the absorption coefficient 'α' with energy near the fundamental absorption edge is expressed as,

$$\alpha_1 = A_1/h\nu(h\nu-E_{g1})^p$$

where, A_1 is the constant depend on the effective mass and the refractive index and p depends on the nature of transition p = ½ for direct transition and p = 2 for indirect transition.

3.2 ELECTRICAL STUDY

In order to study the electrical characterization of $CuGaTe_2$ thin films, dc four probe technique was used. The electrical resistivity measurement was carried out in two different range of temperature a) from 300 K to 473 K and b) from 77 K (liquid nitrogen temperature) to 273 K. The activation energy (E_a) in p-type films can be calculated using the relation,

$$\sigma \alpha \exp\left(\frac{-Ea}{kT}\right)$$

4. RESULTS AND DISCUSSION

4.1 OPTICAL PROPERTIES

Transmittance of the thin films was measured at room temperature using UV-1800 Shimadzu spectrophotometer in the range from 350 nm to 1100 nm. The absorption index (k) and hence the absorption coefficient (α) of the films can be determined from transmittance (T) of the film-substrate alone by fitting the experimental transmission curves to the relation [21],

$$T = A\{ B_1 \exp(\beta) + B_2 \exp(-\beta) + C \cos\gamma + D \sin\gamma \}^{-1}$$

Where $A = 32\, k_0^2 k_s^2 (k^2+k^2)$

$B_{12}=\{(k_0 \pm n)^2 + k^2\}\{(k_s^2 + n_0)(k_s^2+n^2+k+^2) \pm 4\, n_0 n k_s^2\}$

$C = 2\{(k_0^2 - n^2 - k^2)(n^2 - k_s^2 + k^2)(k_s^2 + k_0^2) + 8k^2 k_0^2 k_s^2\}$

$D = 4\, n_o k\{(n^2 - n^2 - k^2)(k_s^2 + k_0^2) - 2k_s^2(k_0^2 - n^2 - k^2)\}$

$\beta = 4\pi kd\lambda$

$\gamma = 4\pi nd/\lambda$

and n_o, n_s are the refractive indices of the surrounding medium (air or vacuum) and of the substrate respectively, λ is the wavelength and d is the film thickness. The absorption coefficient was evaluated using $n_0 = 1$, $n_s = 1.5$, n = 2.84. To calculate exact value of band gap, a graph is plotted between $(\alpha h\nu)^2$ versus hν as shown in fig. 2.The value of band gap energy Eg is determine when this linear portion of the curve extrapolated to $(\alpha h\nu)^2 = 0$, the energy gap is calculated to be 1.23 eV. This value well agrees with the Neumann et al [8] and [22] and Thwaites et al [23] for flash evaporation and from electro reflectance measurement respectively. They have reported the energy band gap was 1.227 eV and 1.24 eV respectively in $CuGaTe_2$ and which corresponds to the transition $\Gamma^4_{7V} \rightarrow \Gamma^1_{6C}$ (the upper index indicates the single group representation from which the state originates)

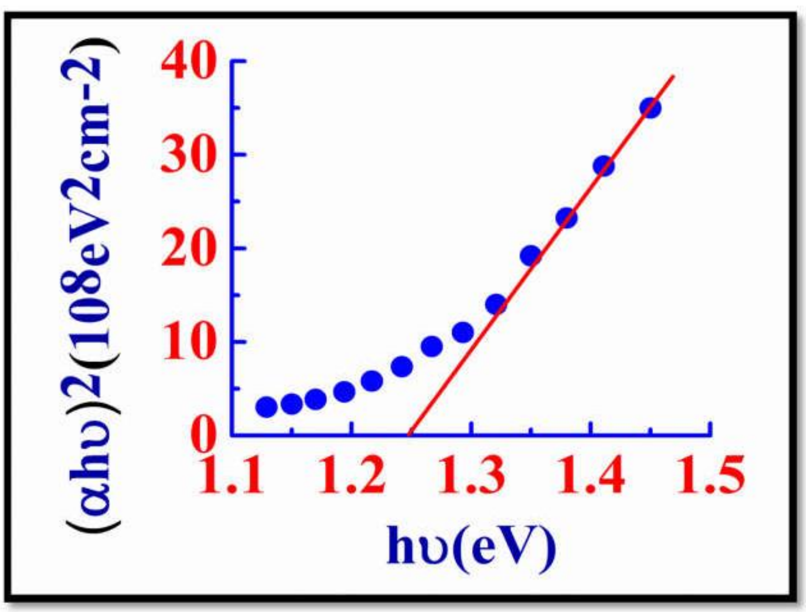

Fig. 2 Plot of $(\alpha h\nu)^2$ against photon energy (hν)

4.2 ELECTRICAL PROPERTIES

The electrical resistivity of the films was measured by four probes technique [14, 24] in two different range of temperature a) from 300 K to 473 K and b) from 77 K (liquid nitrogen temperature) to 273 K. The resistivity for the range a) is measured at atmospheric pressure. The variation of electrical properties of $CuGaTe_2$ thin film formed at different substrate temperature was obtained, a typical Arrhenius plot of conductivity as shown in fig. 3. It is seen from this graph there are three distinct linear regions. The activation energy (E_a) in p-type films can be calculated using the relation,

$$\sigma \ \alpha \ \exp\left(\frac{-Ea}{kT}\right)$$

It is seen from the fig. 2 that the conductivity increases with increasing temperature. However the increase in conductivity is less in the temperature 77 K- 125 K. The activation energy calculated for these three region using the above relation (1) are 115 meV, 45 meV and 6 meV for temperature ranges 300 K- 473 K, 160 K- 250 K and 90 K- 125 K respectively, which are attributed to shallow and deep acceptor states due to copper vacancies. These results are comparable with the reported values [13, 14]. Arrhenius plot can yield the different levels which are responsible for different donor or acceptor mechanism. The films are not doped intentionally and therefore the p-type, acceptor like levels is expected to be present [17].

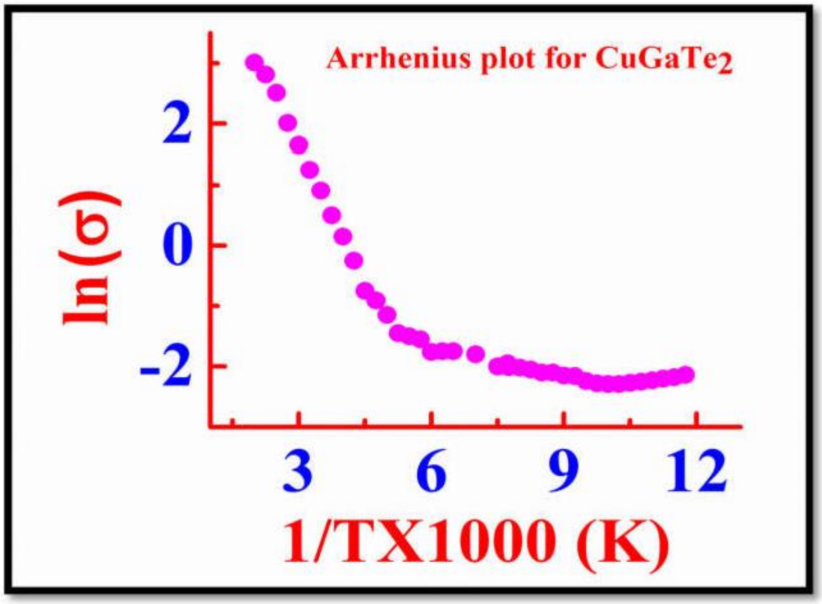

Fig. 3 Arrhenius plot of conductivity of $CuGaTe_2$ thin films

At very low temperature the variable range hopping conduction mechanism appears to be operative [25, 26]. According to Mott [27] phonon- assisted hopping conduction between localized states at low temperature should follow the relation,

$$\sigma = A \exp\left(-\frac{T_0}{T}\right)^{1/4}$$

Where A and T_0 are constants. Fig.4 shows the plot of ln $(\sigma T^{1/2})$ vs $T^{-1/4}$ for the temperature range (77 to 125 K) is linear, which indicate the presence of hopping conduction mechanism. The existence of the localized states necessary for such a conduction process is a consequence of imperfections associated with polycrystalline films [27]. Similar mechanism reported by Sridevi and Reddy [29] for $CuInTe_2$thin films and other workers [15-17, 30].

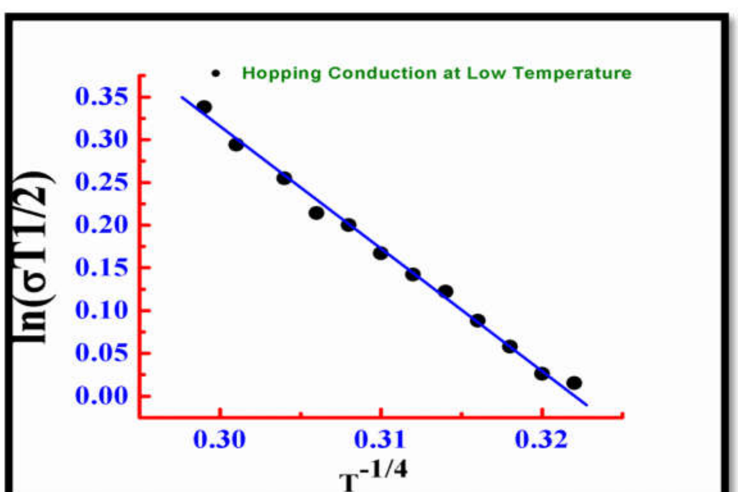

Fig. 4 Plot of ln $(\sigma T^{1/2})$ vs $T^{-1/4}$ showing hopping conduction in $CuGaTe_2$ thin films

4.3 HALL MOBILITY AND CARRIER CONCENTRATION

The Hall coefficient at room temperature was determined by using Van der-Pauw Hall technique [31]. The Hall mobility and carrier concentration at room temperature was found to be 53.34 $cm^2V^{-1}S^{-1}$ and 2.1×10^{19} cm^{-3}. This is because the films formed at these temperature are polycrystalline, single phase and nearly stoichiometric. Our values are well agreed with Reddy et al [32] for flash evaporation techniques, who have reported values 55$cm^2V^{-1}S^{-1}$ and 1.5 $\times10^{19}cm^{-3}$ respectively. Also our values are in good agreed with the results by both these researchers [33] [34] on bulk and thin films of $CuGaTe_2$ material respectively.

5. CONCLUSIONS

We conclude that the spray pyrolytically deposited $CuGaTe_2$ polycrystalline films was p-type, the direct allowed transitions at 1.23 eV are present. The activation energy 115 meV due to the acceptor like levels produced by tellurium interstitials and shallow acceptor levels 6 meV above the valence band. At very low temperature variable range Hopping conduction mechanism appears to be operative.

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