Electrical properties of $CuInTe_{2(1-x)}S_{2x}$ thin film by spray pyrolysis

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Abstract

Thin films of $CuInTe_{2(1-x)}S_{2x}$ were grown by spray pyrolysis and develop thin films on glass substrate at 350C by varying proportion x in the range of 0.25. Aqueous solutions of cupric chloride, indium tri-chloride, thio-urea and tellurium tetra-chloride mixed in proper composition x and studies their electrical properties of all these films. The resistivity of the films was measured for temperature ranging from 77 K to 473 K. The activation energies values were calculated from Arrhenius plot. At very low temperature a variable range hopping conduction mechanism appears to be operative. Surface of thin films has been studied by Scanning Electron Microscope. Copyright © 2018 VBRI Press.

Keywords: $CuInTe_{2(1-x)}S_{2x}$ thin films, spray pyrolysis, electrical properties.

Introduction

Transport phenomenon in I-III-VI ternary group of compound and their solid solutions are as important as their optical properties and they provide valuable information regarding the nature of carriers, band structure and scattering mechanisms. The Hall mobility of charge carriers in the binary compounds are known to be limited by piezo-electric/optical model/impurity scattering in different degree at low temperatures **[1]**. Typical Cu-chalcopyrite-based absorber materials are $CuInTe_2$, $CuInSe_2$, $CuInS_2$, $CuGaSe_2$, $CuScS_2$ and their alloys with band gap in the range of 0.96-1.50 eV **[2, 3]** which is favorable for the solar cell. I-III-VI_2 ternary group of compound are the most popular ternary chalcopyrite semiconductors that have been attracting considerable interest for its direct band gap and high absorption coefficient, which is most suitable for an absorber layer in photovoltaic devices. Thin films of $CuIn(S,Se,Te)_2$ cells with efficiency of 18.8 have been recorded **[4]** while thin films of polycrystalline CIS ($CuInS_2$) solar cells with a conversion efficiency exceeding 14 % have already been achieved **[5, 6]**. CIS thin films have been deposited by various techniques, such as co-evaporation **[7]**, molecular beam deposition **[8]**, reactive magnetron sputtering **[6]**, chemical bath deposition **[9]**, electro-deposition **[10, 11]** and spray pyrolysis **[12, 13, 14]**.

Spray pyrolysis is an attractive method of thin film deposition, as large-area films can be grown economically using this method. In this method, composition of the films is controlled effectively by varying the concentration of the constituents in the spray solution. Versatility of this process makes it suitable for depositing thin films of compound semiconductors. Moreover, spray pyrolysis deposition is a scalable process and hence can be used for depositing large area films which is essential for photovoltaic applications **[15]**.

In the present work, $CuInTe_{2(1-x)}S_{2x}$ thin films were deposited by spray pyrolysis method in an air atmosphere onto glass substrate at temperature of 350°C by varying Te: S ratio and studied their electrical properties by changing the composition parameter x in the temperature range 77 K to 473 K. Hall mobility and carrier concentration also studied. Thickness of the films was measured by Michelson-interferometer. The resistivity of the films was measured by four-probe method and the type of conductivity of the films determined by hot-probe method. So finally we have studied, at above and below room temperature conduction phenomenon takes place due to free electron or holes and hopping conduction mechanism. Therefore, deposited thin films are applications based materials that we have developed and it is operative as a semiconducting device in particular environments.

Experimental

$CuInTe_{2(1-x)}S_{2x}$ films were prepared by spray pyrolysis method. The solutions of (Cupric chloride) $CuCl_2H_2O$ (99%), (Indium tri-chloride) $InCl_3$ (98%), (Tellurium tetra-chloride) $TeCl_4$ (99%) and H_2NCSNH_2 (thio-urea) (99%) of AR grade were prepared 0.02 M of each of the above high-purity compound in distilled water. Here for preparing $CuInTe_{2(1-x)}S_{2x}$ thin films, we have mixed solutions in the ratio 1:1:3.2 by volume, excess tellurium and sulphur was necessary to obtain $CuInTe_{2(1-x)}S_{2x}$ films. Deposited films have occurred tellurium and sulphur deficiency if the ratio of solutions is taken as 1:1:2. Therefore excess of tellurium and sulphur is used to remove this deficiency **[16, 17]**. The solution was sprayed onto heated glass substrate using air as a carrier gas. The spraying rate was maintained 3.5 ml/min. The temperature of the substrate was maintained at 350^0C which was measured by pre-calibrated copper-constantan thermocouple. The distance between the sprayer nozzle and substrate was maintained was 30 cm. The spraying was done in air at 12 kg/cm^2. The glass sprayer moved to and fro to avoid the formation of droplets on hot substrate and to ensure instant evaporation **[2, 3, 12-14]**.

The micro-structural properties were examined by means of scanning electron microscopy, thickness of thin films measure by Michelson interferometer. Electrical conductivity, Hall mobility and carrier concentration also studied. The resistivity of the films was calculated by four-probe method and by hot probe techniques, type of charge carrier (polarity) measured.

Results and discussion

The electrical resistivity of the films was measured by four-probe technique in the range 77 K to 473 K. All the films were found to be p-type which was tested by Hot-probe method. No changes in the type of conductivity were observed when the substrate temperature was changed. Actually the resistivity is determined for two different ranges of temperature ranges (a) from 300K to 473 K and (b) from 77K (liquid nitrogen temperature) to 273 K. The resistivity for range (a) is measured at atmospheric pressure. The resistivity for range (b) is measured at 10^{-2} Torr pressure, for which four-probe arrangement together with the sample film was enclosed in a specially prepared stainless steel container, which was immersed in a liquid nitrogen bath.

Fig. 1 shows the Arrhenius plot of conductivity vs inverse temperature of as deposited $CuInTe_{0.5}S_{1.5}$ thin films. Conductivity (σ) obeys the formula,

$$\rho = \rho_0 \exp\frac{-E_a}{KT} \quad (1)$$

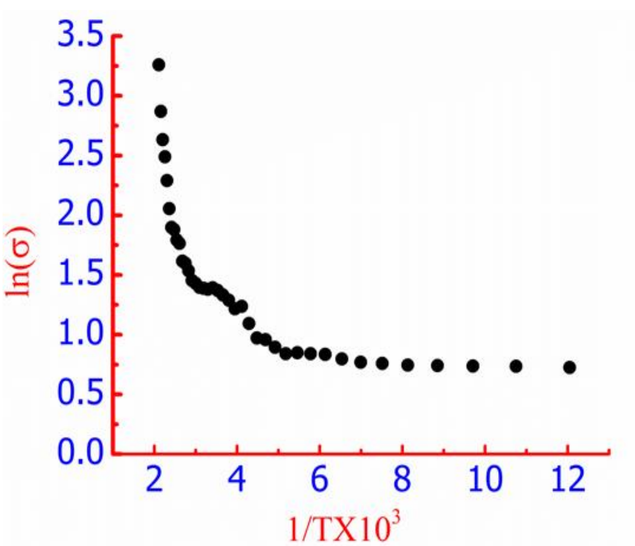

Fig. 1: Electrical conductivity of $CuInTe_{0.5}S_{1.5}$ thin film by Arrhenius plot.

Table 1. Activation energy for different composition(x) at particular temperature range of $CuInTe_{2(1-x)}S_{2x}$ thin films.

Composition (X)	Films	Activation energy (meV) at different temperature		
		300-473 K	160-250 K	90-125 K
x = 0	$CuInTe_2$	60	24	3
x = 0.25	$CuInTe_{1.5}S_{0.5}$	52	18	4
x = 0.5	$CuInTe_{1.0}S_{1.0}$	61	19	7
x = 0.75	$CuInTe_{0.5}S_{1.5}$	100	56	5
x = 1.0	$CuInS_2$	180	70	7

It means that the conduction is due to thermal excitation of holes or electron **[18]**. The Arrhenius plot shows that the atoms are arranged in more regular form **[19]**. Three distinct regions of conductivity are seen. Activation energies calculated for these three regions are 100, 56 and 5 meV for the temperature ranges 300 K-473 K, 160 K-250 K and 90K-125 K respectively. The activation energies were calculated for all composition and tabulated in (**Table 1**).

At low temperatures, where the conduction in the impurity band is due to the thermally activated hopping between localized states, the theoretical model proposed by Cutler and Mott [20] successfully explains the mobility data. The electrical conduction, as mentioned earlier, is mainly by nearest neighbor hopping mechanism in the impurity band (ln σ α 1/T); the electron and hole mobility is analyzed by considering the thermally activated hopping of the charge carriers between localized states in such a band. So, at very low temperature range i.e 90 K to 125 K the activation energy in the range 3 to 7 meV. This is very low activation energy appears to be due to nearest neighbor hopping mechanism in the impurity band. Dawar et al **[21]** also observed hopping conduction below 200 K. Similar mechanism can also present in $CuInSe_2$ and $CuInS_2$ polycrystalline thin film **[2, 3]**. **Fig. 2** shows that the plot of ln ($\sigma T^{1/2}$) vs $T^{-1/4}$ for the temperature 90 K-125K for $CuInTe_{0.5}S_{1.5}$ thin films is linear, which indicates the presence of hopping conduction. Similar result with E_a = 3 meV for flash evaporated $CuInSe_2$ thin films have been reported by Sridevi and Reddy **[22]**.

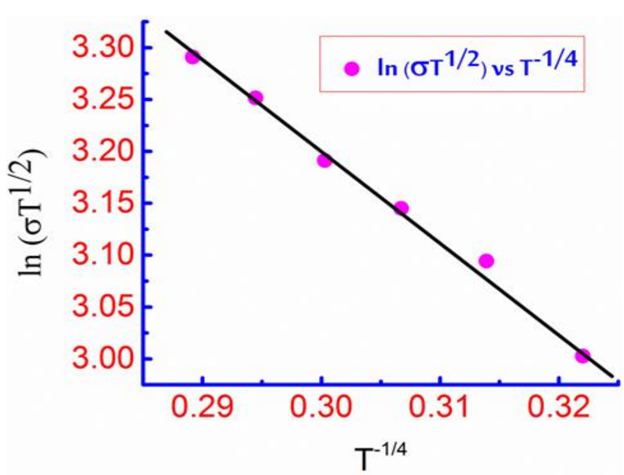

Fig. 2: Plot the graph ln ($\sigma T^{1/2}$) vs T-1/4 of $CuInTe_{0.5}S_{1.5}$ thin film.

Hall mobility of $CuInTe_{2(1-X)}S_{2x}$ thin films for the different composition x at room temperature measured by van der Pauw-Hall technique. Hall mobility is related to the Hall coefficient and it is expressed as,

$$\mu = \frac{R_H}{\rho} \quad (2)$$

Carrier Concentration is given by the relation,

$$p = \frac{1}{|\rho R_H|} \quad (3)$$

where, R_H- Hall coefficient, ρ-resistivity

Carrier concentration, Hall mobility is calculated using above relation (1, 2) and these results were listed in (**Table 2**). From this table, which is agreed well with the reported results by other worker **[21-23]** for $CuInSe_2$, $CuInS_2$, $CuInTe_{2(1-x)}Se_{2x}$, and CuInSTe thin films used by different preparation techniques.

Scanning electron microscopy is a convenient method to study the surface morphology of thin films. Surface morphology of material plays an important role in solar energy conversion efficiency of the device. The SEM micrographs of as-deposited $CuInS_{2(1-x)}Te_{2x}$ thin film on glass substrate at X10,000 and X15,000 magnification for $CuInS_{0.5}Te_{1.5}$ thin film is shown in **Fig. 2**. The $CuInS_{0.5}Te_{1.5}$ thin film has dense, homogeneous and porous growth morphology. The nanosized grains are uniformly distributed throughout the surface. The grains are quite small with equal size and shape, also their boundaries are well defined, and hence it was easy to calculate the exact average value of grain size from SEM image.

Table 2. Electrical parameters of the $CuInTe_{2(1-x)}S_{2x}$ thin films.

Ratio of x	Composition of films	Carrier Type	Hall Mobility (μH) cm^2/Vs	Carrier Concentration (p) cm^{-3}
x = 0	$CuInTe_2$	p	1.57	0.66×10^{19}
x = 0.25	$CuInTe_{1.5}S_{0.5}$	p	1.78	0.95×10^{19}
x = 0.5	$CuInTe_{1.0}S_{1.0}$	p	2.12	1.21×10^{19}
x = 0.75	$CuInTe_{0.5}S_{1.5}$	p	2.68	1.74×10^{19}
x = 1.0	$CuInS_2$	p	6.15	2.33×10^{19}

Conclusion

In summary, $CuInS_{2(1-x)}Te_{2x}$ thin films grown by spray pyrolysis have the same Cu:In atomic ratio as that of the solution and the atomic ratio of Cu:InTe:S in the solution should be 1:1:3.2 to obtain near stoichiometric composition. The dominant intrinsic defects may be due to Sulphur or Tellurium interstitials, acceptor- like levels, 180 meV to 60 meV above valance band and copper vacancies acceptor-like levels, 24 to 70 meV above the valance band. At very low temperature a variable range hopping conduction mechanism appears to be operative. Morphological characterized of $CuInS_{2(1-x)}Te_{2x}$ film for all composition carried out by Scanning Electron Microscope (SEM). SEM pictures (**Fig. 3**) of $CuInS_{0.5}Te_{1.5}$ thin film shows that the particles having spherical or elliptical and uniform deposition onto the substrate. The average grain size was observed to be 268 nm. This observation reveals the films to be microcrystalline in nature.

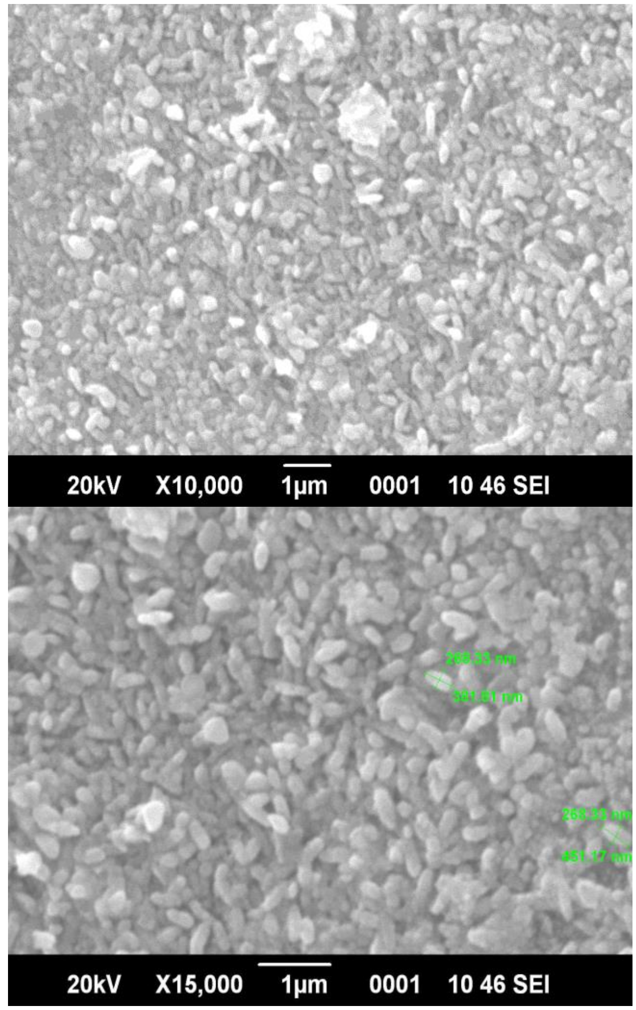

Fig. 3: SEM micrograph of $CuInTe_{0.5}S_{1.5}$ thin film.

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Author's contributions

For this article Anil S. Meshram (Research Student) doing work in lab under the guidance of both this author's named as Dr. Y. D. Tembhurakar, Department of physics, S. K. Porwal College Kamptee (India) and Dr. O. P. Chimankar, Department of Physics, R. T. M. Nagpur University, Nagpur (India). Here for the completion of this financial support of University Grant Commission, New Delhi has awarding MRP Project and Anil S. Meshram doing work as Research Fellow. Major Research Project File No. UGC F. No. 42-808/2013(SR).

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