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Research Paper

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Variation of some physical properties of $CuInS_2$ films by substrate temperature

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Abstract- Spra***y*** pyrolysis is one of the most convenient, economical, inexpensive and simple methods for depositing large area semiconducting thin films. Semiconducting ternary $CuInS_2$ thin films have been deposited onto the glass substrate by varying substrate temperature from 275^0C, at the interval of 25 to 350^0C by using aqueous solution of Cupric chloride, Indium tri-chloride and thiourea of 0.02 M and Seems to be one of the more important parameters affecting the physical properties of the semiconductor. The lattice parameter a and c at room temperature of the tetragonal unit cell were calculated for all these samples by Bruker AXS D8 Advance X-ray diffraction (XRD) techniques with Cu K_α (wavelength = 1.5418 Å) radiation.Conductivity of thin films determined by Four Probe method and hot probe technique wasdetermined to exhibit p-type conductivity. Due to temperature effect, shows the atoms are arrange regular in compound of these samples prepared at various temperatures 250, 300 and 350^0C. As the films are not doped intentionally defect observed in intrinsic nature operative to be produced by Sulphur interstitials. Grain sizes were studied by Scanning Electron Microscope.

Keywords-*Spray pyrolysis; $CuInS_2$ Ternary Semiconductor; XRD; Four Probe Technique*

I. INTRODUCTION

In recent years, the development of nano-structural I-III-VI_2 ternary compound semiconducting materials in the form of thin films occupy a prominent place in basic research and solid state technology due to their expanding range of potential applications in the diverse field such as photovoltaic cells, electronic components, fabrication of large area photodiode arrays, photoconductors, sensors, antireflection coatings, optical filters, surface acoustic wave devices, solar selective coatings and solar cells etc [1, 2].

$CuInS_2$ is one of the I-III-VI_2 chalcopyrite-type mixed crystal semiconductor. $CuInS_2$ as an absorber layer is very promising for thin film photovoltaic applications [3], which matches well with the solar spectrum,its high absorption coefficient of approximately 10^5 cm^{-1} and its direct band gap energy obtained from 1.40 - 1.53 eV [3-5] and high absorption coefficient [6] and its controllable conduction type. In the recent years the ternary group compounds have high conversion efficiency that exceeds 12 to 19 %. This means that CIS/Se/Te-based solar cells are able to complete with poly si-based solar cells even though their cost of production is high. Several techniques have been investigated to prepare $CuInS_2$ thin films. Thin films of ternary compound have been prepared by several methods such as evaporation [7-9], electro-deposition [11] [12], chemical bath deposition [13] and spray pyrolysis [5, 6, 14-22]. Electronic structures were reported by Jaffe and Junger [23], there are fundamental role to deep study with support (ideal) to all new researchers.

All the researchers have deal with the determination of structure type and qualitative observation of defects and grain size of $CuInS_2$ thin films [22]. No quantitative measurements were made on the micro-structural parameters of pyrolytically deposited $CuInS_2$ thin films. The micro structural parameters such as crystallite size, strain and dislocation density are found to influence the physical chemical properties of spray pyrolytically deposited $CuInS_2$ thin film may be useful for opto-electronic applications. The main advantage of the technique is that just by varying the substrate temperature; it is possible to control stoichiometry of the deposits. The film growth rate depends on the number of parameters like temperature of the substrate, duration of spray, the solution spray rate and pH of the solution. The influences of temperature on the structural and electrical properties of thin films are very important.

In present study, we are reported varying substrate temperature and characterized by X-ray Diffraction, Electrical properties and results have been presented.

II. RELATED WORK

In addition to this, $CuInS_2$ have prepared by simple and low cost chemical spray pyrolysis method. It gives a good quality semiconductor which allows fabrication of solar cells with satisfactory efficiency due to their unique properties such as less material need and better device performances [24]. $CuInX_2$ belong to the I-III-VI_2 group of semiconducting compound where x = Se/S/Te. These materials crystalline with the chalcopyrite structure and can be regarded as valance analogous of the II-VI compounds. $CuInX_2$ has recently attracted a lot of interest because of its potential for use in solar cells [1] and photovoltaic detectors [2]. The electrical properties of $CuInX_2$ have been described by several authors and it appears that the conductivity type is established through defect doping mechanism. The electrical properties of I-III-VI_2 compounds are believed to be dominated by the presence of intrinsic defects such as Cu, In and Se/S/Te vacancies and interstitials.

III. METHODOLOGY

3.1 PREPARATION OF SAMPLES OF THIN FILMS

The deposition was carried out onto commercially available glass substrates of the size (7.5 ×2.5×0.1) cm^3. The $CuInS_2$ thin films were prepared by spraying an aqueous solution of copper chloride ($CuCl_2$) of purity 99 % MERCK Company, indium tri-chloride ($InCl_3$) of purity 98 % HIMEDIA Company, tellurium tetra-chloride ($TeCl_4$) of purity 99 % HIMEDIA Company and thiourea [$(NH_2)_2CS$] of purity 99 % MERCK Company on biological glass substrate kept temperature at 275, 300, 325, 350 and 375^{0}C. All these films were deposited by taking equimolar aqueous solutions of $CuCl_2$, $InCl_3$, $TeCl_4$ and thiourea in appropriate value to obtain Cu: In: Te and Cu: In: S for 1:1:3.2 [25**]**. The excess elements were used to remove deficiency of VI group elements [26]. Stock solutions of 0.02 M of each of the above compounds were prepared in double distilled water and the starting solution was mixed thoroughly and sprayed [15, 22, 25 and 27-28]. The substrates cleaning plays an important role during the deposition process, therefore, the substrates were cleaned with distilled water, acetone and take on the hot plate. The atomization of the chemical solution into a spray of fine droplets is elected by the spray nozzle, with the help of compressed air as carrier gas [29]. The sprayed droplets on reaching the hot substrate undergo pyrolytic decomposition and form a single crystal, cluster, or crystallites of the product. The pressure in air compressor was measures by pressure gauge and the distance between sprayer and glass substrate was about 25 -30 cm. Substrate temperature was controlled by means of Copper-constantan thermocouple. The spray rate was about 3-5 ml/min through the sprayer ensures a uniform film thickness [22]. A biological glass slides (7.5 cm X 1.5 cm X 0.1 cm), was used as substrates, and placed in a fitted socket at the surface of a substrate heater when sprayed. The glass sprayer was mechanically moved to and fro during spraying to avoid formation of droplets on the hot substrate and to ensure instant evaporation [28]. Process time was ranging between 20 and 60 min depending on the solution amount.In order to find optimized condition for deposition of $CuInS_2$ thin films, the depositions were carried out by varying one of the parameters as substrate temperature and keeping the others at fixed value. The sprayed droplets on reaching the hot substrate undergo pyrolytic decomposition and form a single crystal, cluster, or crystallites of the product. The experimental set-up we used for our sprayed process is diagrammed in Figure 1, and it has been details described in references [5, 6 and 28-29].

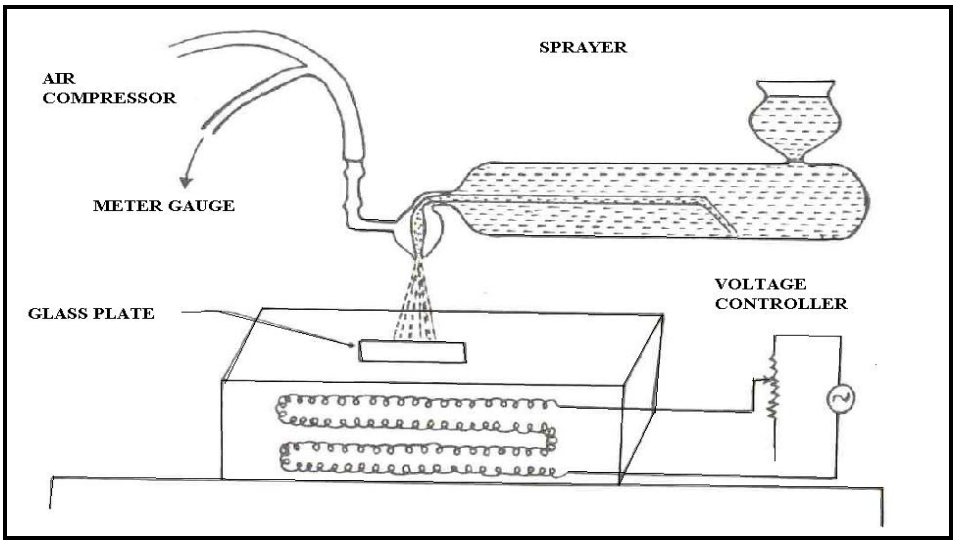


Figure 1 Schematic diagram of chemical spray pyrolysis unit [5]

3.2 INITIAL INGREDIENT

1) Copper Chloride ($CuCl_2$. $2H_2O$) = 170.48 gm/mole
2) Indium Tri-chloride ($InCl_3$) = 221.18 gm/mole
3) Tellurium Tetra-chloride ($TeCl_4$) = 279.41 gm/mole

3.3 CHARACTERIZATION OF $CuInS_2$ THIN FILMS

3.3.1 STRUCTURAL ANALYSIS

The structural characterization of the films were carried out by analyzing the XRD patterns obtainedusing X-ray diffraction was taken on Bruker AXS D8 Advance X-Ray Diffractometer, with Cu Ka (l = 1.5418 Å) radiation and maximum usable range 3 to 135 degree.
Thickness of the films was measured by Michelson-interferometer.

3.3.2. ELECTRICAL ANALYSIS

Electrical resistivity calculated by Four-probe technique with Van der Pauw technique of cross shaped samples was tested for the measurement of Hall mobility and carrier concentration of all these films.

3.3.3. SURFACE MORPHOLOGICAL AND COMPOSITIONAL ANALYSIS

The SEM images of as deposited $CuInS_2$ thin films at different temperature (250 to 375^0C at the interval of 25^0C) was taken scanning electron microscopy (JEOL Model JSM-6390LVEDS for 20 volt) coupled with energy dispersive spectrometer (EDS) and by Inductively coupled plasma atomic emission spectrophotometer (ASCAES) Analysis. Torch temperature was 8000- 10,000 K and wavelength used for Cu- 324.754 nm, In- 230.678 nm, Te- 203.562 nm and S-213.211 nm respectively.

IV. RESULTS AND DISCUSSIONS

4.1. STRUCTURAL PROPERTIES

The chemical spray pyrolytically as-deposited $CuInS_2$ thin films at various temperatures possess tetragonal chalcopyrite structure. It is confirmed by comparing the peak positions (2θ) of the XRD patterns of the films with the standard X-ray powder diffraction data (File 65-2732). Figure 1 (typical figures 250, 275, 300, 325, 350 and 375) shows the X-ray diffraction pattern obtained of as depositedat different substrate temperatures (275^0Cto 350^0Cat the interval of 25^0C) of $CuInS_2$ thin films. The observed diffraction peaks of $CuInS_2$ thin film prepared at 350^0Cwere found at 2θ values of angles 25.113^0, 28.888^0, 33.292^0, 39.281^0, 44.64^0, 49.90^0, 59.88^0, 72.23^0, 76.53^0corresponding to the lattice planes (112), (200/400), (211), (301), (116/312), (231/107), (235/413) and (420/404) respectively. The different peaks in the x-ray diffraction were indexed by usual method. The corresponding values of inter-planar spacing'd' were calculated and compared with chalcopyrite phase standard JCPDS data [30].

Table 2 and 3 present the calculated d values, other internal parameters and the corresponding indices, respectively. XRD studies revealed that the films of $CuInS_2$ are polycrystalline in nature with chalcopyrite structure of these films was confirmed with lattice constant (a = 5.5507Å and C= 11.090Å). The degree of preferred orientation increased and shifted with the substrate temperature and with thickness. Thus, raising the substrate temperature did not lead to the formation of other phases. It is seen that as temperature/thickness increased the peaks intensity found to increases and shifted indicating better crystalline form. In fact, the film prepared at the highest temperature, 350^0C, has a better crystalline quality, as indicated from its XRD spectra.

It is observed from Figure 2 that the height of the preferential peak increases, that films to be well crystalline with preferential orientation along (112) direction and some new peaks of $CuInS_2$ begins to appear while increasing temperature from 350 to 375^0C, there after the height of the preferential peak slightly decreases. Hence, the films deposited at 350^0C have good crystallinity and well adherent to the substrates.

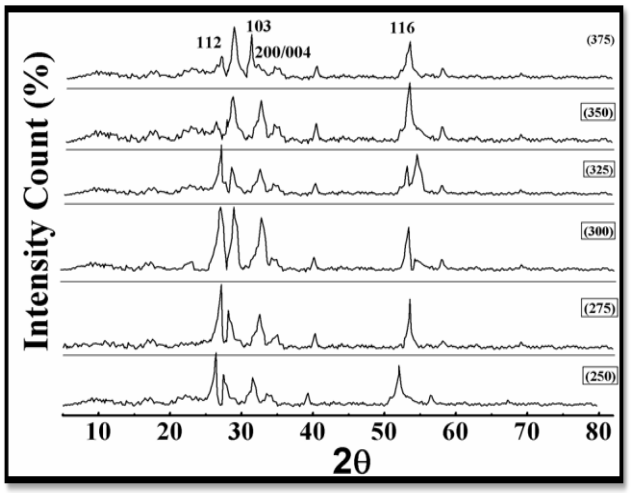


Figure 2 X-ray diffraction patterns obtained of as deposited $CuInS_2$ thin films at different substrate temperatures

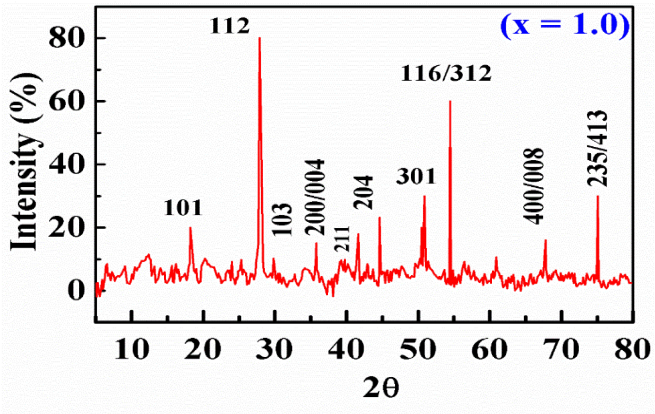


Figure 3 X-ray diffraction pattern obtained of as deposited at different substrate temperatures 350^0C of $CuInS_2$ thin films

It may also observe that initially films nucleated in a random orientation. There is growth of nuclei in initial temperature level free energy values minimum because at minimum free energy surface with growth rate of the crystal plane in certain temperature [31]. The particle size can be obtained larger than the calculated from XRD crystallite size (Scherrer equation). The crystallite size of the films was calculated to be in the range 7.2 – 8.5×10^{-10}m and tabulated all these (other parameters) values in Table (2 and 3). SEM photograph which are helps to actual ideas about the range of particle size Fig. It is also seen that the crystallite size decreases at temperature for the higher thickness which may be attributed to developed a new children grain on the surface of greater grains and lesser in Full-width in half maxima with the best orientation of the plane (112) which are recommended greater unique results [32].

However, many researchers [20, 33, 34, 21] using spray pyrolysis and different techniques, obtained a single phase of tetragonal chalcopyrite crystal of $CuInS_2$ thin films.Our calculated values of lattice parameter well agree with results reported by other workers [20, 34 and 35].

Table 2 Structural parameters of $CuInS_2$ thin films as deposited various substrate temperatures

T (^{0}C)	Thick-ness (t) (µm)	(hkl) Planes	2θ	(d) Cal	JCPDS File (65-2732)	
					(d) Std	2θ
250	0.1432	112	26.44	3.3709	-	-
		103	27.45	3.2491	-	-
		200	31.53	2.8373	-	-
		116	52.02	1.7579	-	-
275	0.1686	112	26.55	3.3572	-	-
		103	27.63	3.2283	-	-
		200	31.785	2.8152	-	-
		116	52.13	1.7544	-	-
300	0.1733	112	26.65	3.3498	-	-
		103	28.45	3.1371	-	-
		200	32.125	2.7861	-	-
		116	53.14	1.7234	-	-
325	0.1752	112	27.81	3.207	-	-
		103	29.06	3.0726	-	-
		200	32.172	2.7822	-	-
		116	54.452	1.6850	-	-
350	0.2862	112	27.90	3.1977	3.1987	27.869
		103	29.12	3.0665	3.0734	29.030
		200	32.189	2.7807	2.7700	32.292
		116	54.832	1.6742	1.6704	54.922
375	0.1756	112	27.93	3.194	-	-
		103	30.33	2.9468	-	-
		200	33.90	2.6442	-	-
		116	55.12	1.6661	-	-

The grain size (D) was calculated using Debye-Scherror formula from the full width at half maxima (FWHM) [36] [22][19].

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

$$D = \frac{0.94\,\lambda}{\beta \cos\theta} \quad (2)$$

Here, λ is the wavelength of source radiation, k is the Scherror constant having a value 0.94, β is the FWHM of the peak corresponding to (112) plane and θ is the Bragg's angle.

The lattice constant (a and c) and inter-planner spacing (d) values for the tetragonal structure is determined by the relation (eq. 3),

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \quad (3)$$

The crystallographic parameters like lattice constant (a and c), inter planer spacing (d), crystallite size (D), Internal strain (ε), dislocation density (δ) and number of crystallites per unit area (N) were calculated and tabulated in Table 2.

Table 2 Thickness and structural parameters of $CuInS_2$ thin films as deposited various substrate temperatures

T (^{0}C)	Thick-ness (t) (μm)	(hkl) Planes	2θ	Crystal-lite Size (D) (10^{-10} m)	Dislocation Density (δ) (10^{11}) (m^{-2})	Strain (ε) (10^{-4})	Lattice Constant (10^{-10} m)		Number of Crystallites (N) (10^{11}) (m^{-3})
							a	c	
250	0.143	112 103 200 116	26.44 27.45 31.53 52.02	7.552	1.753	1.678	5.676	10.963	3.323
275	0.168	112 103 200 116	26.55 27.63 31.78 52.13	1.488	0.451	0.103	5.630	10.916	5.109
300	0.173	112 103 200 116	26.65 28.45 32.12 53.14	0.633	0.024	0.140	5.572	10.715	0.681
325	0.175	112 103 200 116	27.81 29.06 32.17 54.45	0.635	0.024	0.137	5.564	10.429	0.681
350	0.286	112 103 200 116	27.90 29.12 32.18 54.83	0.041	6.149	5.800	5.561	10.392	2.876
375	0.175	112 103 200 116	27.93 30.33 33.90 55.12	0.901	1.232	7.270	5.288	10.215	0.240

The strain (ε), dislocation density (δ) and the number of crystallites per unit area (N) of the films calculated using the formulae [36] [22],

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad (4)$$

$$\delta = \frac{1}{D^2} \quad (5)$$

$$N = \frac{t}{D^3} \quad (6)$$

The dislocation density (δ) internal strain (ε) and number of crystallites per unit area (N) values changes with respect to rise in temperature and these values varied in the range of (1.84- 1.17×10^{10}m), (4.92-1.19×10^{-6} m^{-2}) and (3.84–$2.89\times10^{8}m^{-3}$) respectively. Strain in all these films are

calculated from full-width of half maxima [22] of the prominent peaks (112) appears in XRD. Here all these parameters are found to be decreased for higher temperature of the films due to the low crystallinity or no vacancies are formed (no misfit location at higher temperature 375^{0}C).

In spray pyrolysis technique, the starting materials required to form the desired compound are taken in the form of solutions, which are then mixed and sprayed onto preheated substrates resulting in thin films on the surface of substrates. When the droplets of the sprayed solution reach the hot substrate, owing to pyrolytic decomposition of the solution, well adherent and good quality films of $CuInS_2$ are formed on the substrates.

4.2 THICKNESS VARIATION

The majority of film thickness on structural, optical magnetic and electrical properties of thin films is very important. Many reports already done on the effect of size on thin films of various aspects of materials have been published [19, 22]. The thickness of the films deposited at various substrate temperatures was measured by gravimetric method and its variation with substrate temperature is shown in fig. The thickness increases with increase in temperature, attains the maximum value at 350^{0}C and then decreases for further increase in substrate temperature (Figure 4). At lower temperatures (<350^{0}C), the temperature may not be sufficient to decompose the sprayed droplets from the solution and therefore the deposit results into a low thickness.

At substrate temperature 350^{0}C, the deposition occurs at optimum rate resulting in terminal thickness of 0.2 m. at higher substrate temperature (>350 ^{0}C), film thickness decreases due to higher evaporation rate from initial ingredient. Variations in thickness of the films deposited at various temperatures such as 275^{0}C, 300^{0}C, 325^{0}C, 350^{0}C and 375^{0}C are shown in Figure 1. It is clear that the film thickness increases with increasing temperature. This increase may be attributed to the structural characteristics of films.

Table 3 Comparative thickness of the $CuInS_2$ films

T (^{0}C)	**Thickness (µm)**	
	Michelson Interferometer	Weighing Method
250	0.1432	0.147
275	0.1686	0.164
300	0.1733	0.175
325	0.1752	0.173
350	0.1862	0.184
375	0.1756	0.172

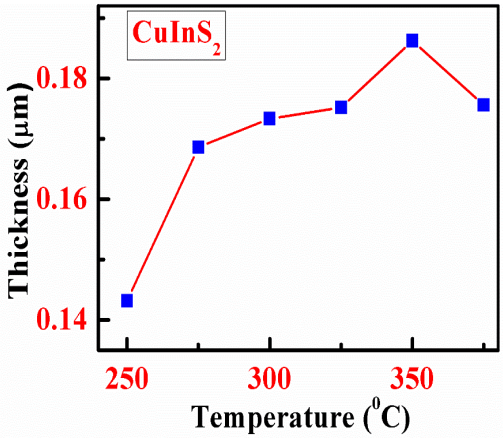


Figure 4 Thickness versus temperature of $CuInS_2$ thin films of Different temperatures

4.4 ELECTRICAL ANALYSIS

The measurement of p-conductivity (σ) and activation energy (E_a) was carried out one by one of all the films of $CuInS_2$ by using the four probe technique [37] [22]. The van der Pauw Method is a great practical technique commonly used to measure the resistivity and the Hall coefficient of a sample using cross shaped sample geometry to eliminate finite contact effects [37] and provide gold ohmic contact [38]. Its power lies in its ability to accurately measure the properties of a sample of any arbitrary shape, so long as the sample is approximately two-dimensional (i.e. it is much thinner than it is wide) and the electrodes are placed on its perimeter.The resistivity was measured at room temperature for all the films prepared at different temperature 250, 300 and 350^{0}C at the interval of 50^{0}C. Hot probe method showed p-type conductivity, it indicates the copper rich in films [19, 22]. Conductivity increases with increasing temperature of as-deposited thin films [39]. The high-temperature slope is connected to the band conductivity (hole or electron) whereas the low temperature one to the hopping conductivity over the localized states of impurity band (hopping Conduction). The resistivity is determined for two different ranges of temperature range (a) from 300 K to 473 K and range (b) is from 77 K to 273 K. The resistivity for range (a) is measured at atmospheric pressure, conductivity obeys the formula of equation (eq. 7 and 8), and meaning that the conduction is due to the thermal excitation of electron or holes. The resistivity for range (b) is measured at 10^{-2}torr pressure for which a four-probe arrangement together with sample film was enclosed in a specially prepared stainless steel container, which was immersed in a liquid nitrogen bath.

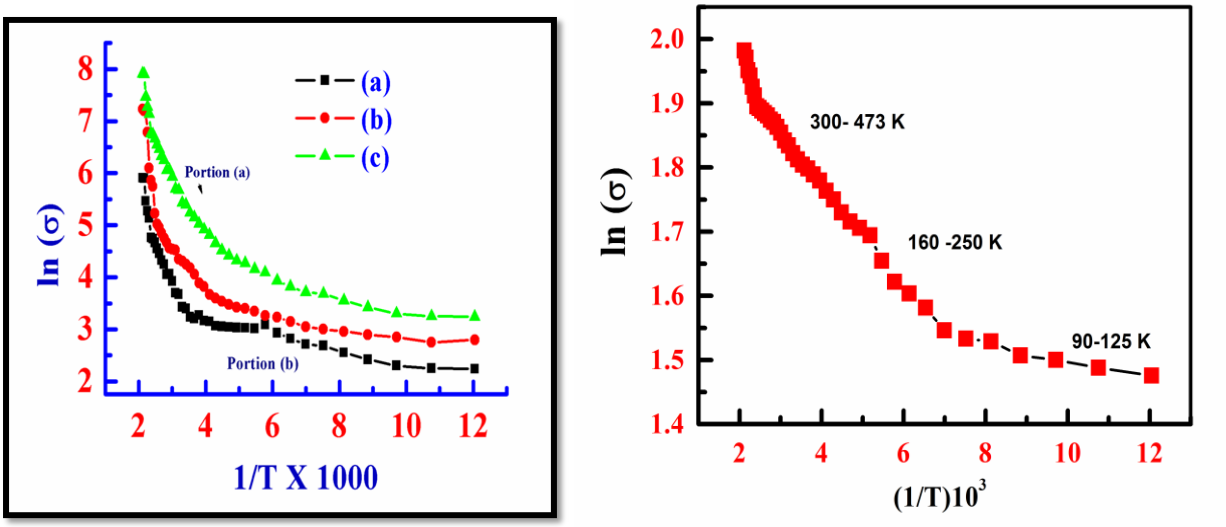


Figure 5 Arrhenius plot of conductivity versus inverse temperature of as deposited at various temperatures (a) 250, (b) 300 and (c) 350^{0}C respectively

Figure 2 (a, b and c) shows the typical Arrhenius plot of conductivity versus inverse temperature of as deposited at various temperature [37]. Figure 2 (a) (b) and (c) show the variations in resistivity and thickness with substrate temperature, at a fixed spray rate of 3.5ml/min. The decrease in film thickness is attributed to a decrease in the deposition rate of initial constituent with increasing substrate temperature. This change in resistivity may be attributed to change in the density of free electrons and change in mechanism of scattering at the surface of nano-structured films due to grain boundaries. At higher temperature (350^{0}C), the films showed that the atoms are arranged in more regular form than as deposited films.The resistivity was calculated for two different ranges of temperature: - Range (I) is from 300- 473 K and range (II) is from 77 K (liquid Nitrogen temperature) to 273 K using relation given below,

$$\rho = \frac{\pi t}{\log_e 2} \times \frac{V}{I} \qquad (7)$$

It was observed from Figure 5 (c) that three distinct regions of conductivity are seen.The resistivity of the films was found to decrease as the substrate temperature increases. This decrease may be attributed to the growth of the grain size and the improvement in film stoichiometry as indicated by the XRD pattern in Figure 2. This is in accordance with Xu et al. [12] who suggested that higher substrate temperatures lead to larger grain size and a smooth surface. The order of resistivity in the present work obtained is in the rangeof 10^3–10^5 Ωcm, which is suitable for solar cells. These results of resistivity are quite similar to those obtained by Hussain et al [33], Yukawa et al [40] and Bandyopadhyaya et al [41], on electrodeposited and stacked element layerfilms by a modified source. The activation energy (E_a) in p-type film can be calculated using the relation,

$$\sigma \alpha \exp(Ea/kT) \qquad (8)$$

The activation energies were calculated from these given graph and straight line plots. Activation energies calculated using above equation for these three regions (from Figure 7) are 100-180 meV, 37-70 meV and 5-10meV for the temperature range 300 -473 K, 160 - 250 K and 90 - 125K respectively and these values are tabulated in Table. 4. The Arrhenius plot can yield the different levels which are responsible for different donor or acceptor mechanisms. The change in the carrier mechanism is indicated by the change in slope of the curve [42]. The activation energy of 180-100meV obtained higher energies in our investigation is agreed well with 88 meV calculated by hydrogenic approximation which may be due to the acceptor like levels produced by Sulphur interstitials at high temperature regions above 250 K. It is also observed that different scattering mechanism [37] [42] are operative in two temperature regimes (for high temperature). Our values are nearly equal to the Sridevi and Reddy [43] who was reported activation energy 100 meV for the temperature range 250 K to 300K for flash evaporated $CuInS_2$ thin films. Films are may be or may not doped intentionally and therefore the defect observed in intrinsic nature. The conductivity values were slightly higher order than previous results by other workers [39]. Contribution of magneto-Conductivity in three different constituents system present in the materials. First one corresponds to weak interaction, second due to electron electron interaction and third one arises due to weakly disordered electron gas arising from spin orbit splitting of conduction electron energies [44**].** In $CuInS_2$ at the temperature range 150- 300 K, the grain boundary effect is also present, for this graph oflog ($\sigma T^{1/2}$) versus ($1/T\times10^3$) is

plotted (Figure 6). The plot is a straight line which indicated the predominance of grain boundary effect in this temperature range [8].

According to Mott [45] phonon- assisted hopping conduction between localized states at low temperature should follow the relation [46],

$$\sigma = A\exp(-T_0/T)^{1/4} \quad (9)$$

Where, A and T_0 are constants. Figure 7 shows that 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 [46].

Table 4 Activation energies calculated from Arrhenius plot of as-deposited $CuInS_2$ thin films at various temperatures

T(^{0}C)	Activation Energy of $CuInS_2$ thin films deposited at various temperatures in three distinct regions		
	300-473 K	160-250 K	90-125 K
250	100	37	10
300	142	58	8
350	180	70	7

The existence of the localized states necessary for such a conduction process is a consequence of imperfections associated with polycrystalline films [22] [39]. The activation energy for this temperature range is 7-10 meV. This value are smaller than Amara et al [8] who has reported activation energy 16.50 meV, for thermally evaporated polycrystalline thin films of $CuInS_2$ in the range of Temperature from 77 to 300K. They observed hopping conduction below 200 K. Similar mechanisms were reported by Sridevi and Reddy [43] for $CuInTe_2$ thin films and also by other workers [11, 47] for $CuInSe_2$ thin films for sprayed and thermally evaporated method respectively.

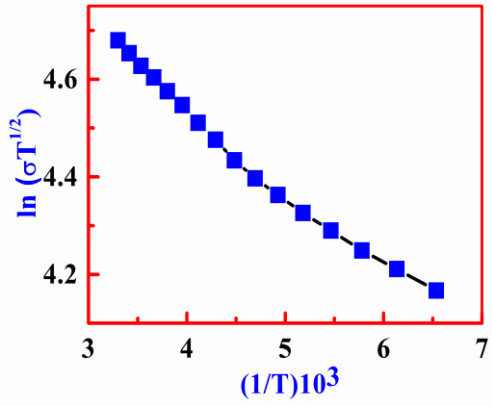


Figure 6 Plot of $\ln(\sigma T^{1/2})$ versus temperature showing grain boundary effect in $CuInS_2$ thin films

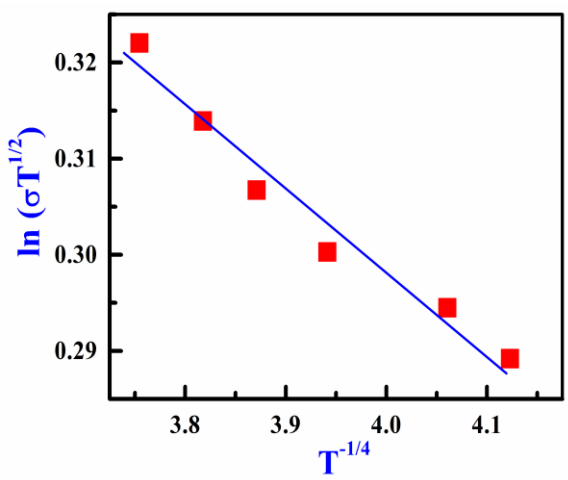


Figure 7 Plot of $\ln(\sigma T^{1/2})$ versus $T^{-1/4}$ showing hopping conduction in $CuInS_2$ thin films

It is seen that all these compounds are stoichiometric. Hence the compounds $CuInS_2$ are completely miscible in all properties. It is also observed that each was slightly indium rich [48]. Dawer et al [49] studied the similar works on vacuum deposited $CuInS_2$ thin films in the temperature range 77 K to 300 K. They stated that the films would have a large deficiency in copper than indium which consistent with higher carrier concentration. Since the films are polycrystalline, the activation energy compounds to the potential barrier of the grain boundary.

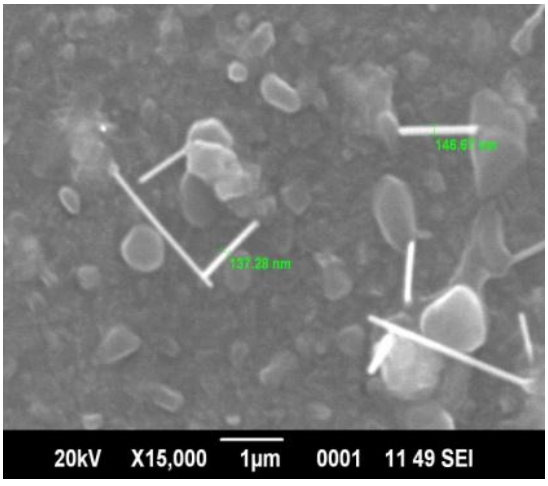
4.5 MOBILITY AND CARRIER CONCENTRATION OF $CuInS_2$ THIN FILMS

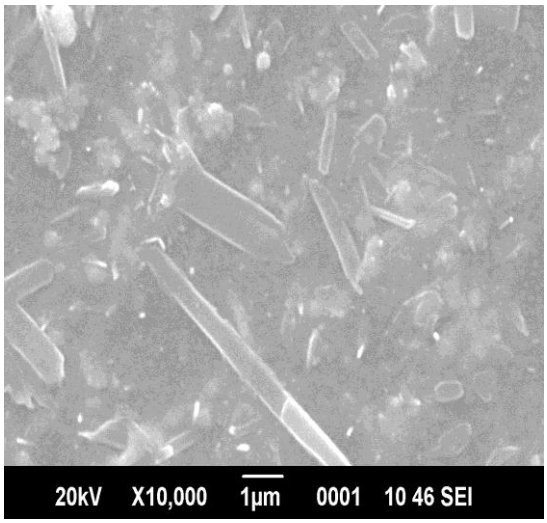
The Hall coefficient of $CuInS_2$ thin films at room temperature was determined by using the Van der Pauw Hall technique [45]. The Hall mobility (μ_H) and carrier concentration varied between 6.15- 8.40 $cm^2V^{-1}s^{-1}$and 2.2 – 7.2 × 10^{19} cm^{-3} for $CuInS_2$ thin films prepared at different temperatures (250, 300 and 350^{0}C).This is because the films formed at these temperature are polycrystalline, single phase and nearly stoichiometric. The Hall coefficient of this sample was positive, confirms the p-type conductivity by using hot probe method. As expected the conductivity and mobility values are found to be slightly less upon other temperature (250^{0}C) of the films due to recrystallization phenomena just start and the also reduction of the grain boundaries. Mobility and concentration values of this samples are found due to relatively low amount of disorder of cation vacancies (Cu and In) and disorder of lattice sites [48]. Ours values well agreed with Kazmerski [50] and other researchers [51] for vacuum evaporation method. They observed Hall mobility in the range 10-30 $cm^2V^{-1}s^{-1}$ [6]. By Wahab et al [32] [43] were fabricates $CuInS_2$ thin films material by thermal evaporation method and studied their electrical dc conductivity and activation energy in the temperature range between 150-300^{0}C. The conductivity

values were between 76.6 Sm^{-1} to 631.26 Sm^{-1} and there activation energies were calculated to be in the range 0.05 to 0.08 eV. In earlier works [35] on I–III–VI_2 semiconductors, the samples used were deep into the insulating side of themetal–insulator transition (MIT), with carrier concentrationstwo to three orders of magnitude below the criticalconcentration. In last decade VRH conduction was mainlystudied in elementary and binary semiconductors. Semiconductors of the groupI–III–VI_2 are $CuInS_2$, $CuInSe_2$ and $CuInTe_2$ [35, 46]. A crossover conduction from Mott to ES VRH behavior, by lowering temperature, was reported in $CuInTe_2$ [35, 52] down to 0.4 K. In Cu-ternaries VRH conduction occurs at relatively high temperatures of up to.

4.6 SURFACE MORPHOLOGICAL AND COMPOSITIONAL ANALYSIS

Scanning Electron microscopy images of as-deposited $CuInS_2$ thin films shows, as the temperature varied 250 to 350^{0}C, the grain are in homogeneous, uniform and less defect grains are appeared [39]. At low temperature (250^{0}C) little beat of grains are misfit and found number of dislocation and the structure of the grains appeared like a tube and Choco-bar like structure are seen in figure 8. As the thickness value varies grain size also varied with them. Average grain sizes of all these films are 140- 268 nm. It means all these grain boundary structural particles are obtained in nano- size [19, 39]. The energy dispersive spectrum and inductively coupled plasma atomic emission spectrophotometer (ASCAES) Analysis of as deposited $CuInS_2$ thin films of thickness 0.1862 µm is also indexed in Table 5. These results represent the average value of two different regions. According to EDS and ASCAES results all sprayed films are sulfur rich and contain Cl contamination up to 2-4 %. Presence of chlorine is due to the use of chloride based precursors for deposition.





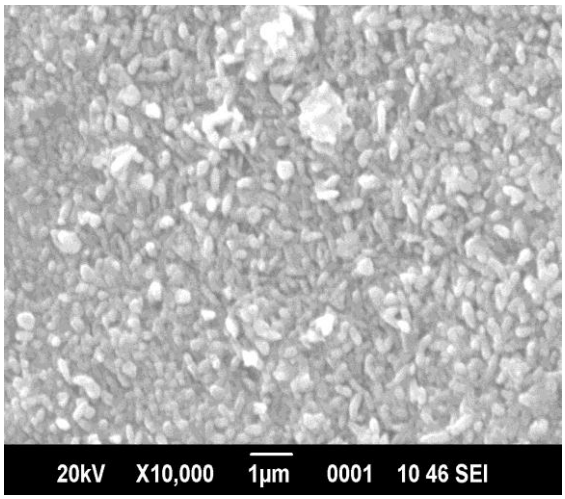


Figure 8 SEM Micrograph of $CuInS_2$ thin films prepared at various temperatures (1) 250 (2) 300 and (3) 350^{0}C respectively

Table 5 Percentage atomic concentration

T (^{0}C)	Percentage atomic concentration					
	EDS Analysis (%)			(ASCAES) Analysis (%)		
	Cu (%)	In (%)	S (%)	Cu (%)	In (%)	S (%)
250	25.211	26.325	48.464	25.312	24.842	48.846
300	24.890	25.141	49.969	25.642	25.424	48.934
350	25.812	25.520	48.668	24.985	25.312	49.703

V. CONCLUSION

The $CuInS_2$ thin films have been successfully prepared by a simple and inexpensive spray pyrolysis deposition method.The structural, electrical and optical properties of nanostructured $CuInS_2$films were investigated. The XRD spectra of the sample showed tetragonal structure with preferred orientation along 112 directions. The good crystallinity was found obtained at higher substrate temperature (350^0C) of the sample. The conductivity of the films of p-type was obtained. The films are not doped intentionally hence the defect observed in intrinsic nature. The acceptor like levels are appears to be produced by sulphur interstitials. The SEM images of the $CuInS_2$ thin films shows good compound formation. The resistivity of the as-deposited films was found to vary in the range 10^3-10^5 Ωm, depending on the substrate temperature. Conductivity studies reveal the semiconducting nature of the films. An evolution of p-type conductivity is obtained in temperatures 250, 300 and 350^0C which requiresfurther investigations. From the SEM analysis we examined, the average grain size was varied in the range of 140- 168 nm and has found thickness values decreases at higher temperature. It is also observed that grain boundaries effect governthe electrical transport of the charge carriers in polycrystalline $CuInS_2$ thin films, for higher and lower temperature. It clearly also seen that there is formation of number new children grains with regular and uniform in size. Comparative elemental compositional study reveals of EDS and ASCAES results confirmed that elemental composition of the films did not change major affected with amount of precursor solutions. So that, the all these films are developed in proper concentration ratio.

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