Synthesis, Structural and Optical Characterization of Spray-Deposited $CuInS_2$ Thin Films

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Abstract

Polycrystalline nano-structured $CuInS_2$ thin films have been prepared by chemical spray – pyrolysis of aqueous solution of Copper Chloride, Indium Chloride and Thiourea onto heated glass substrate. The structural, morphological, optical absorptions properties of the $CuInS_2$ thin films have been systematically studied to understand the effect of various preparative parameters like substrate temperature, Tc, Hydrogen ion concentration (pH) and ion ratio (Cu/In) of the spray solution. It is observed that the parameters critical to structural and optical properties of sprayed $CuInS_2$ films are substrate temperature and ion ratio of Cu/In in the spraying solution. The X-ray diffraction patterns confirm that the use of copper rich solutions reduce the temperature required for single phase composition of $CuInS_2$ films from 375 ^{0}C (Cu/In = 1.0) to 300 ^{0}C (Cu/In = 1.2). The absorption coefficient α was calculated from transmittance and reflectance measurements over a large spectral range (300 – 2500 nm). The optical data have been analyzed to evaluate the optical band gap. The average film thickness and refractive index were calculated from ellipsometeric data.

Keywords: $CuInS_2$ thin films, Spray pyrolysis, Structural properties, SEM, Optical properties, Film thickness.

1. Introduction

The two principal requirements for a thin film solar cell material are high conversion efficiency and low fabrication costs. Several promising materials are currently being investigated at various research laboratories in an effort to improve properties and to reduce process costs. Among the semiconducting ternary compounds I-III-VI_2 with chalcopyrite structure, $CuInX_2$ (X = S, Se) are more promising materials for photovoltaic application. These I-III-VI_2 ternary semiconductor compounds have been grown and investigated in single-crystal form by several research groups [1-5]. The compounds of the class $CuInX_2$ (e.g. X = S, Se, Te) have also gained special interest for possible device applications. For large scale economic utilization it is desirable to produce these ternary compounds in thin film form. $CuInSe_2$ has been widely studied because of the quite good efficiency obtained with solar cells using the compound as absorbing layer. However, if it's electrical properties are suitable for photovoltaic application its optical band gap (1.02 eV) is quite small, the optimum value for the solar spectrum being 1.45 eV. In addition to this there has been apprehension for use of selenium on ecological reasons. One possibility is to substitute Se by S. The optical band gap of $CuInS_2$ (1.4 eV) matches well with the solar spectrum. Therefore, it is desirable to prepare $CuInS_2$ thin films which should be carefully characterized to understand the reasons that may help to improve their performance for applications.

A variety of techniques have been used to deposit $CuInS_2$ thin films, such as single source evaporation [6], co-evaporation from elemental sources [7], electrodeposition [8] and spray pyrolysis [9,10]. A multisource evaporation technique has resulted as the best ternary compound solar cells on the basis of $CuInSe_2$ [11]. Other inherently less expensive thin film deposition techniques do not provide and reproducible compositional control of deposited films [12]. Additional heat and chemical treatments are required to improve the qualities of thin films [13,14]. Chemical spray pyrolysis is an attractive method and large-area films with good uniformity can be grown at low cost. Recent activities on CSP study are low due to the low conversion efficiency (up to ~ 6%) of the cells on the basis of as-deposited sprayed $CuInSe_2$ films [15]. There are still many preparative parameters in CSP technology, which need to be addressed [16,17].

Chemical spray deposition or spray pyrolysis is a process for preparing thin film from a wide variety of materials. This process was developed in the early 1960s by Hill and Chamberlin [18] for preparing thin polycrystalline films from binary photoconductors such as CdS and CdSe and their solid solutions and was later studied by a number of other investigators [19]. In the present study, the chemical spray pyrolysis (CSP) method is applied to deposit $CuInS_2$ thin films. The spray pyrolysis process involves spraying a solution, usually aqueous, containing soluble salts of desired compound's constituent atoms onto a heated substrate. This method offers a way for the deposition of transparent conducting thin films. It is of particular interest, because of its simplicity, low cost, and minimal waste product. This method allows the coating of large area and it is easy to include in an industrial production. In spray pyrolysis, the precursor solution is sprayed directly onto heated substrate. A stream of gas (e.g. compressed air) is used as carrier gas to help the atomization of the solution through the spray nozzle.

The structural and optical properties of sprayed $CuInS_2$ films depend on the preparation conditions such as growth temperature and ion ratio of Cu/In in spraying solution. The preparative parameters have been optimized to obtain phase pure homogeneous single phase polycrystalline thin films. This paper reports on the thin film deposition and their structural, morphological and optical properties.

2. Experimental

2.1 Experimental Techniques

Figure 1 shows the schematic representation of the chemical spray pyrolysis setup used for the growth of $CuInS_2$ thin films. In the present study, Copper Chloride ($CuCl_2$) (AR), Indium Chloride ($InCl_3$) (AR) and Thiourea ($(NH_2)_2$ CS) (AR) were used as starting materials. Deionized water was used for solutions. $CuInS_2$ thin films were prepared by spraying of aqueous solution of ($CuCl_2$ + $InCl_2$ + 3 SC $(NH_2)_2$) with the concentration of 1 mmol/1 Cu^{2+}. Copper to Indium molar ratio in the solution was varied in the range of Cu/In = 1.0 – 1.2. In order to change Cu/In, the concentration of $CuCl_2$ was changed, keeping concentration of $InCl_3$ and thiourea constant. The pH value of spray solution used in this study was 4.0 in order to prevent the precipitation of $InCl_3$ and thiourea. Prior to the spray deposition, N_2 gas was passed through the solution to displace dissolved oxygen. An excess of thiourea was necessary in the final solution. Thiourea was chosen as the source of sulfur ions in the spray solution because it avoids the precipitation of metallic sulfides and hydroxides since it forms complexes with copper and indium ions easily. The solutions were sprayed onto glass substrate. In this work microscopic glass slides (75 mm x 25 mm x 1.1 mm Blue Star make) were used as substrates. The substrate temperature was varied between 300 – 350 ^{0}C. In order to obtain most durable, adherent and uniform coatings on glass support, the substrate surface must be free from contaminants such as grease, adsorbed water, dust particles etc. The durability is dependent on many factors other than surface cleanliness alone. But this is the basic requirement for obtaining clean, contaminant free coatings. The gross contaminants were first removed by detergent solution. These slides were cleaned with redistilled water and then agitated in ultrasonic cleaner for about 20 minutes. The slides were then rinsed thoroughly several times in redistilled water and later subjected to vapour degreaser using pure alcohol; A.R. grade isopropyl alcohol was used for this purpose. These clean slides were used as substrates for deposition.

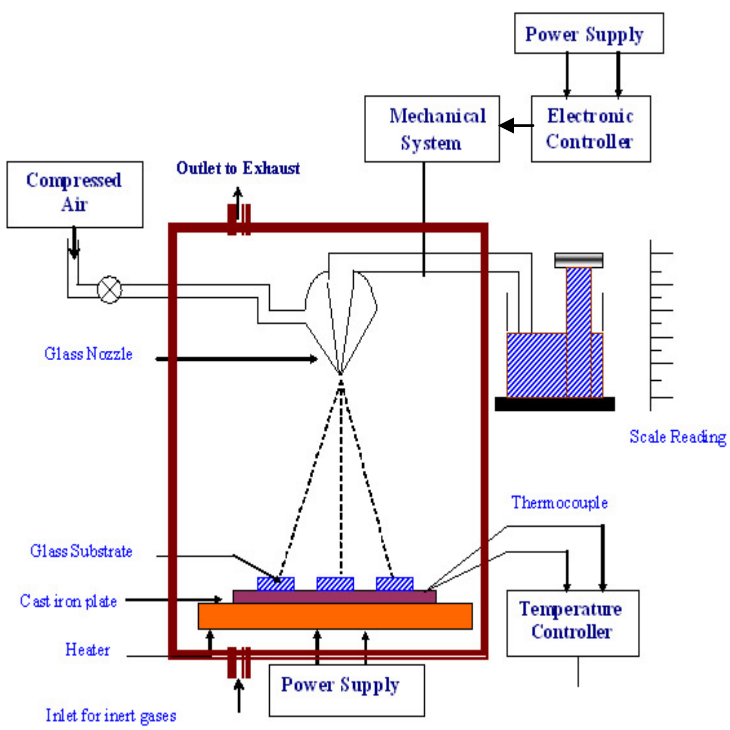

Figure. 1 Schematic representation of the chemical spray pyrolysis setup used for the growth of $CuInS_2$ thin films.

2.2 Spray Pyrolysis Details

$CuInS_2$ thin films were prepared by using spray pyrolysis technique. The growth chamber was filled with Nitrogen and subsequently substrate temperature was raised up to the desired value. For all experiments, the solution spray rate was 2 ml/min while the carrier gas flow rate was 1 lit/min. In all cases the deposition time was 10 min. The substrate temperature Ts, during the deposition was used as parameter with 580K <Ts <650 K. the air flow rate: 8LPM and solution flow rate: 10ml/min. The average film thickness changed between 0.4 to 0.6 µm.

2.3 Characterization Techniques

The deposited films were characterized for their structural and optical properties. X-ray diffraction (XRD) patterns of sprayed films were recorded using monochromatic CuK_α radiation (λ = 1.5418 A) in a wide range of Bragg angles 2θ ($10^0 \le 2\theta \le 80^0$) with a scanning rate of 0.02 ^{0}C was employed to obtain the diffraction pattern of the films. The average particle size of the samples were obtained from the X-ray peak width (FWHM) using Scherrer's formula [20]. The X-ray data were analyzed to obtain interplaner spacing and unit cell parameters of the phase present. The changes in the intensity of some prominent peaks with the variation of processing parameters like substrate temperature and concentration were used to obtain the nature of orientation of the grains formed in the films. This orientation was estimated from the variation of $I_{(hkl)}/I_{max}$, with the processing parameters. The surface morphology of the films was examined by scanning electron microscopy (SEM). SEM studies were carried out using JOEL - JSM - 5600 SEM instrument. The scanning electron microscopy technique provided the structural information of the surface of the thin film deposited with a wide range of magnification in one dimension.

The optical transmittance and reflectance spectra was recorded in wavelength range of 300 – 1100 nm using spectraphotometer "SCHIMADZU" model – UV 160 A. The absorption coefficient α was calculated from transmittance T and reflectance R measurements by using **–**

$$\alpha = \frac{1}{t}\ln\left[\frac{(1-R)^2}{T}\right] \quad \text{----------------------------- (1)}$$

where t is the thickness of the film. Transmittance and reflectance measurements at near normal incidence were performed over a large spectral range (300 – 1100 nm) on $CuInS_2$ films deposited on glass substrates. These measurements were undertaken to compare the optical performance of $CuInS_2$ films prepared at different substrate temperature T_s. The transmittance (T) and reflectance(R) spectra obtained for $CuInS_2$ films deposited at different substrate temperatures (T_s) was used to obtain the values of absorption coefficient α and hence to evaluate the optical band gap from the plot of $(\alpha h\nu)^2$ Vs photon energy. The data indicate that the direct band gap was approximately of the order of 1.46 eV. The average film thickness was measured with an ellipsometer.

3. Results and Discussion

3.1 X – ray diffraction (XRD) studies:

The phase purity and structure of the sprayed films was obtained from the analysis of the XRD patterns of the deposited films. All the sprayed films were characterized at room temperature by X-ray diffraction using CuKα radiation. The X-ray analysis revealed that all the films possessed single phase as seen from the absence of impurity peaks. The X-ray peaks were indexed and unit cell parameters were obtained using least squares programme. All the diffractograms of the prepared films clearly indicated polycrystalline nature $CuInS_2$ films. The peak intensity ratio $I_{(hkl)} / I_{max}$ gave a measure of preferential orientation. The preferential orientation was obtained from the intensity of the (112) peak. The unit cell parameters a and c of the tetragonal phases were calculated using least squares fit analysis. The calculated values of lattice parameter a = 5.5 39 $\pm$ 0.002 Å, c = 11.092 $\pm$ 0.002 Å were found to be in good agreement with the values reported for $CuInS_2$ with chalcopyright structure. The average particle size was calculated from full width at half maximum (FWHM) the intensity of Bragg peak (112). The film consisted of crystallites with sizes in the range between 50 to 100 nm. Figures 2 a, b and c show the XRD patterns of $CuInS_2$ thin films prepared at different substrate temperature (300^0C to 375^0C) for Cu/In ratio 1.0, 1.1 and 1.2 respectively. The XRD analysis (Fig. 2a) showed that the increase in the growth temperature leads to polycrystalline $CuInS_2$ thin films. The temperature required for single phase growth depends on Cu/In in the solution For Cu/In = 1.0 the films exhibit diffraction peaks belonging only to $CuInS_2$ (PDF 27-159) at growth temperature Ts = 375 ^{0}C. It was also observed that with increasing growth temperature the (112) peak become sharper. Using copper rich solution Cu/In > 1 single phase film was obtained at lower temperature 350 ^{0}C and 325 ^{0}C for 1.1 & 1.2 respectively. $CuInS_2$ films grown using copper rich starting solution Cu/In= 1.1 or 1.2 were found to have tetragonal chalcopyrite structure (PDF 27-159) confirmed by the splitting of (116/312) reflection and by weak (103) reflection. The formation of chalcopyrite structure of ternary compound was explained by additional energy required to order the atoms from disordered sphalerite phase [19]. Present results showed that copper excess in the solution had strong effect to the formation of chalcopyrite structure. The Tables 1, 2 & 3 summarized the interplaner spacing and intensity of (112) peaks. Thickness and refractive index of $CuInS_2$ films is given in Tables 4, 5 & 6.

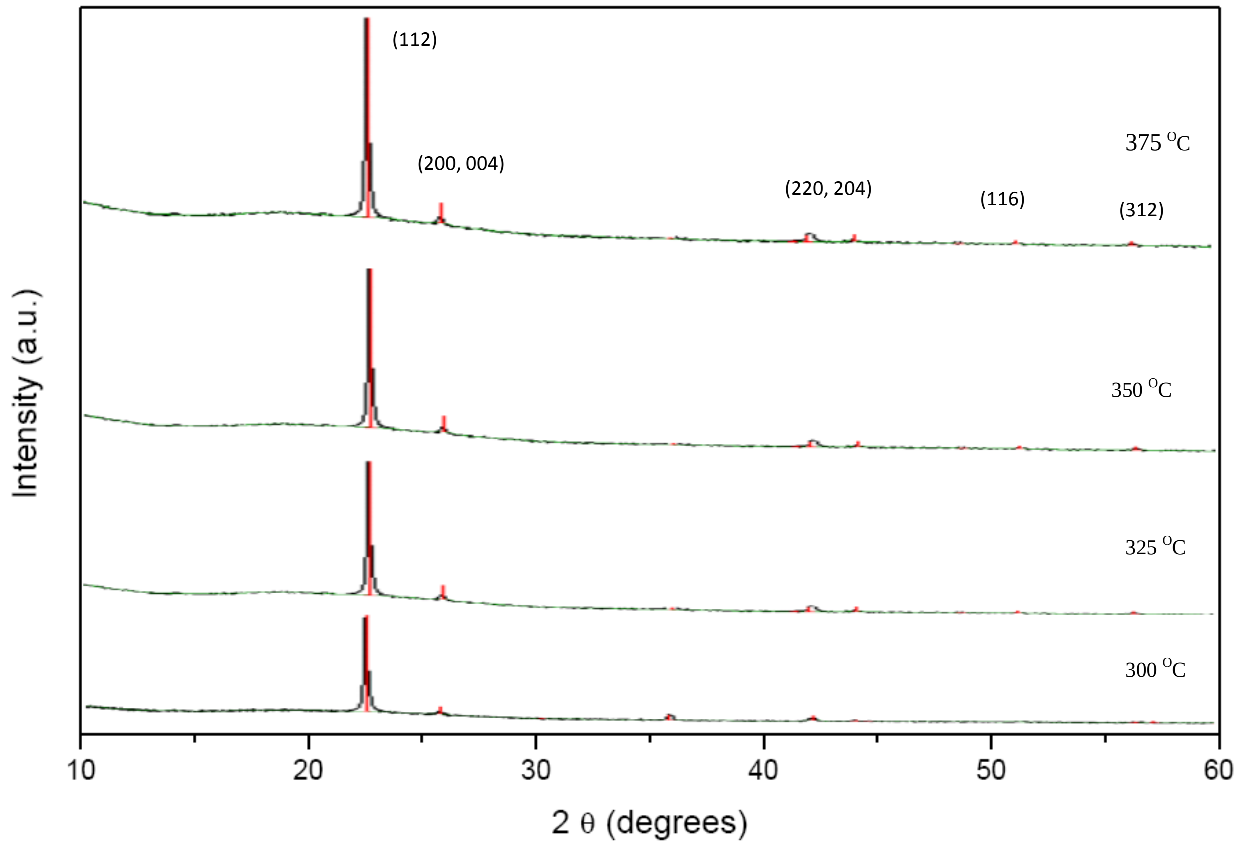

Figure. 2a X-ray diffraction pattern of $CuInS_2$ thin films prepared at different temperature with spraying solution Cu/In = 1.0

Tables 1 Influence of the substrate temperature on the structural and optical properties of $CuInS_2$ film of Cu/In = 1.0

T_s (^0C)	d_{112}	I_{112}	Eg (eV)
300	3.1960	100.00	1.39
325	3.1976	100.00	1.40
350	3.1976	100.00	1.42
375	4.6583	100.00	1.44

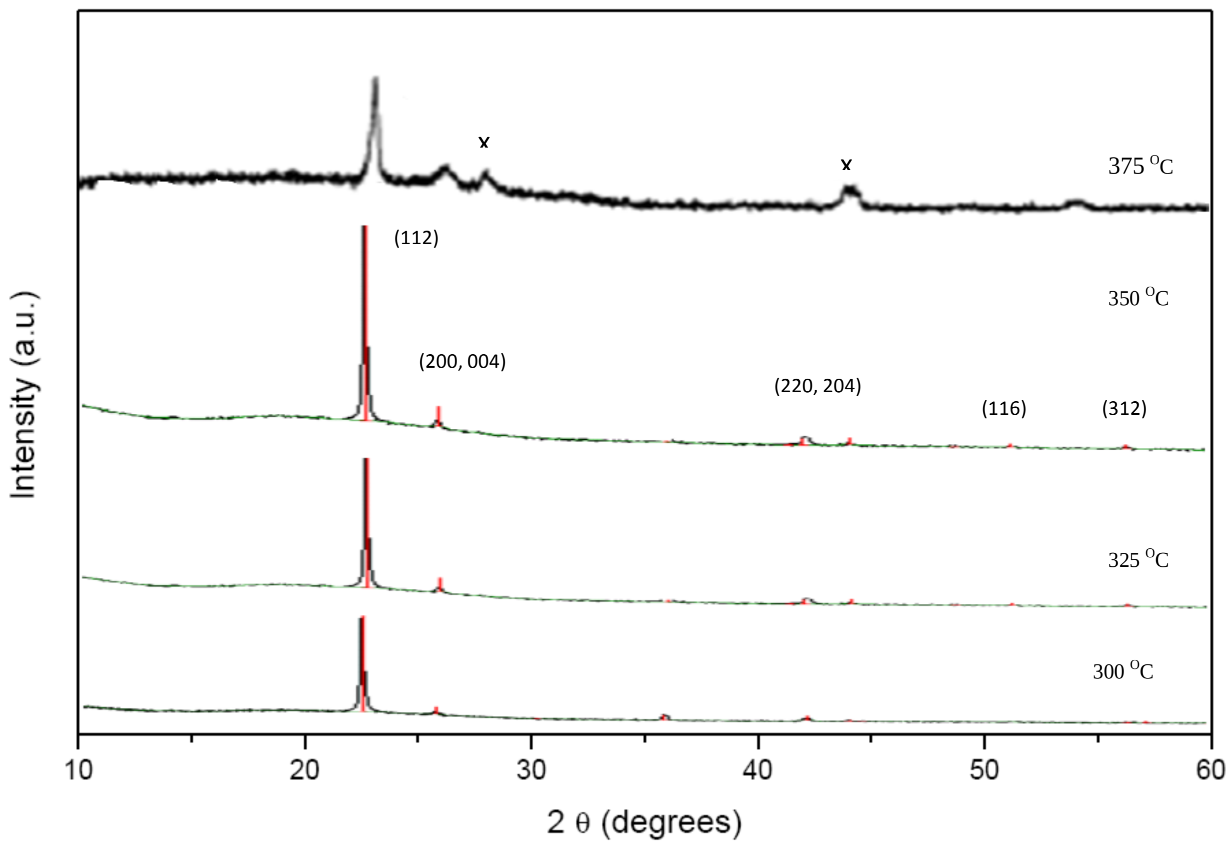

Figure. 2b X-ray diffraction pattern of $CuInS_2$ thin films prepared at different temperature with spraying solution Cu/In = 1.1

Tables 2 Influence of the substrate temperature on the structural and optical properties of $CuInS_2$ film of Cu/In = 1.1

T_s (°C)	d_{112}	I_{112}	Eg (eV)
300	3.1911	100.00	1.30
325	2.8207	100.00	1.25
350	2.8200	100.00	1.32
375	2.8170	100.00	1.37

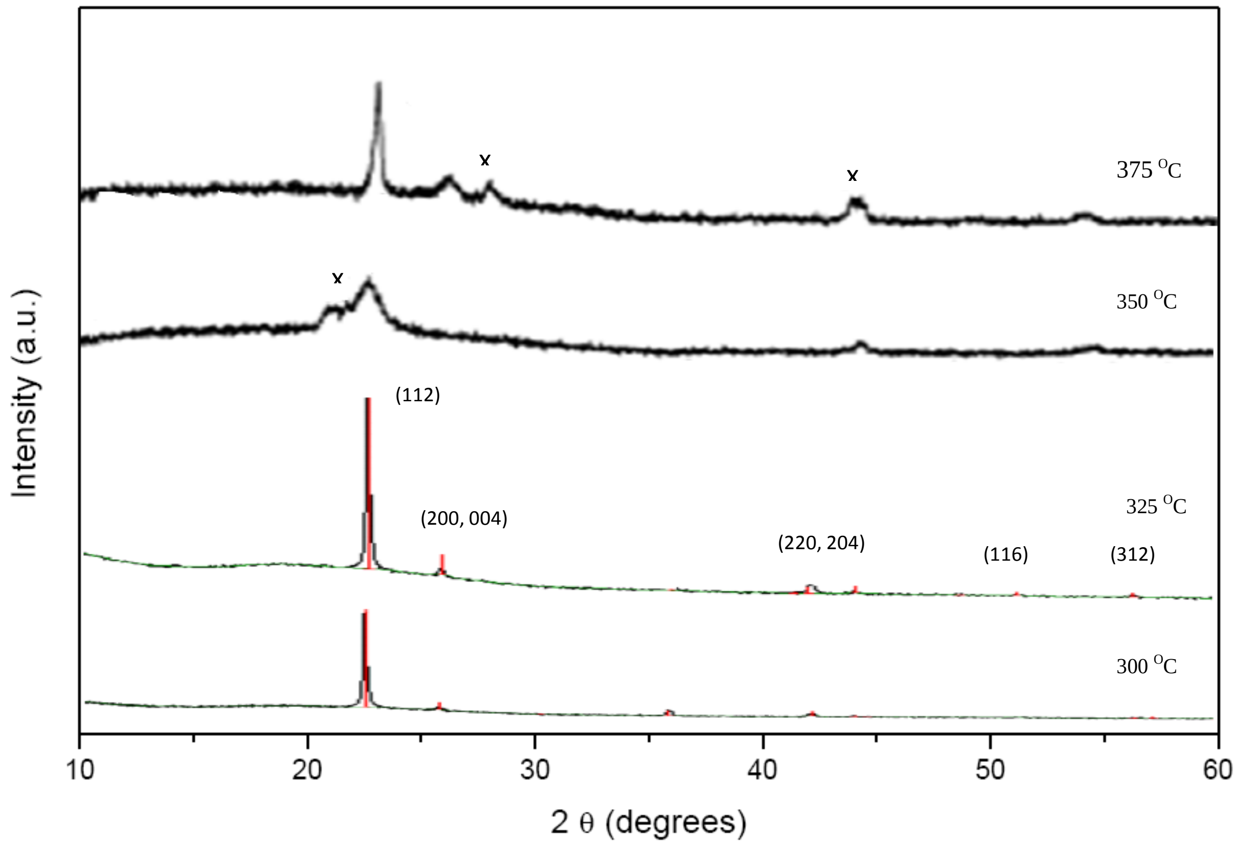

Figure. 2c X-ray diffraction pattern of $CuInS_2$ thin films prepared at different temperature with spraying solution Cu/In = 1.2

Tables 3 Influence of the substrate temperature on the structural and optical properties of $CuInS_2$ film of Cu/In = 1.2

T_s (^{0}C)	d_{112}	I_{112}	Eg (eV)
300	3.19108	100.00	1.29
325	3.20100	100.00	1.32
350	3.19382	100.00	1.33
375	3.19409	100.00	1.35

Tables 4 Thickness and Refractive Index of $CuInS_2$ film for Cu/In = 1.0

Substrate Temp (^{0}c)	Thickness (Ǻ)	Refractive Index
300	5204	2.412
325	5117	2.526
350	4994	2.848
375	4290	2.317

Tables 5 Thickness and Refractive Index of $CuInS_2$ film for Cu/In = 1.1

Substrate Temp (^{0}c)	Thickness (Ǻ)	Refractive Index
300	5173.22	2.464
325	5091.71	2.683
350	4992.93	2.814
375	4822.09	2.645

Tables 6 Thickness and Refractive Index of $CuInS_2$ film for Cu/In = 1.2

Substrate Temp (^{0}c)	Thickness (Ǻ)	Refractive Index
300	5173.22	2.464
325	5091.71	2.683
350	4992.93	2.814
375	4822.09	2.645

Figure 3 shows the typical scanning electron micrograph of $CuInS_2$ thin films. Fig. 3 A,C,E (300 ^{0}C) & Fig. 3 B,D,F (375 ^{0}C) with Cu/In =. 1:0, 1.1 &1.2 showed very smooth surface. The increase in the substrate temperature leads to growth of crystallite size. These micrographs showed films of two distinct morphology. At low substrate temperature (< 300 ^{0}C) solid phase of the precursor was deposited with less transmittance (A, C & E), while micrographs of films formed at higher deposition temperatures showed a uniform film nature with distinct grain growth boundaries. The films deposited at 375 ^{0}C (B, D & F) consisted of uniform crystallites in the form of small grains. The film grown at 300 ^{0}C showed crystallites with sizes in the range 40 - 80 nm (Fig. 3

A,C,E) while the films grown at 375 ^{0}C consisted of sharp-edged crystallites with sizes of 50 - 200 nm (Fig. 3 B, D, F). The surface morphology of the films changed from smooth to more roughness and the transmittance decreased due to light scattering. The stoichiometric composition in starting solution (Cu/In) had very strong influence on the microstructure and surface morphology of the films. Copper-rich starting solution promoted the formation of the films with larger well-defined crystallites at lower growth temperatures. The film grown at 320 ^{0}C (Cu/In = 1:1) showed the formation of separate crystals on the film surface (Fig. 3 E). The increase in the temperature leads to the growth of the size of crystallites in the film as well separate crystals on the surface.

Absorption coefficient and band gap values for spray $CuInS_2$ thin films were determined from the optical transmission data. Figures 4 a, b & c depicted the optical transmission spectra of the films deposited at various deposit temperature for different Cu/In ratio 1.0, 1.1 & 1.2. The highest optical transmission was obtained in the films grown at 300 – 375 ^{0}C for all the films deposited with different Cu/In ratio. The absorption coefficient α is calculated using the above relation (1). The value of absorption coefficient (α) at various wavelengths was calculated and found to be dependent on both radiation energy and composition. The cutoff of the transmittance spectra towards short wavelengths indicated the onset of the intrinsic interband absorption in the $CuInS_2$ layer and the sharpness of the absorption edge increases with the substrate temperature. For an allowed direct band gap transition the absorption coefficient is related to the photon energy hν by

$$\alpha h\nu = A\,(h\nu - E_g)^{1/2} \quad \text{------------------------} \quad (2)$$

where A is a constant and E_g is the energy gap. For a direct band gap semiconductor the $(\alpha h\nu)^2$ versus hν characteristic is predicated to be a straight line with a photon - energy axis intercept giving the value of the band gap. A typical plot of $(\alpha h\nu)^2$ against the photon energy hν for the films deposited at 350^{0}C is presented in Figure 5.The band gap Eg = 1.46 eV was obtained from extrapolated intercept with the hν axis and tabulated in Table 1, 2 & 3.

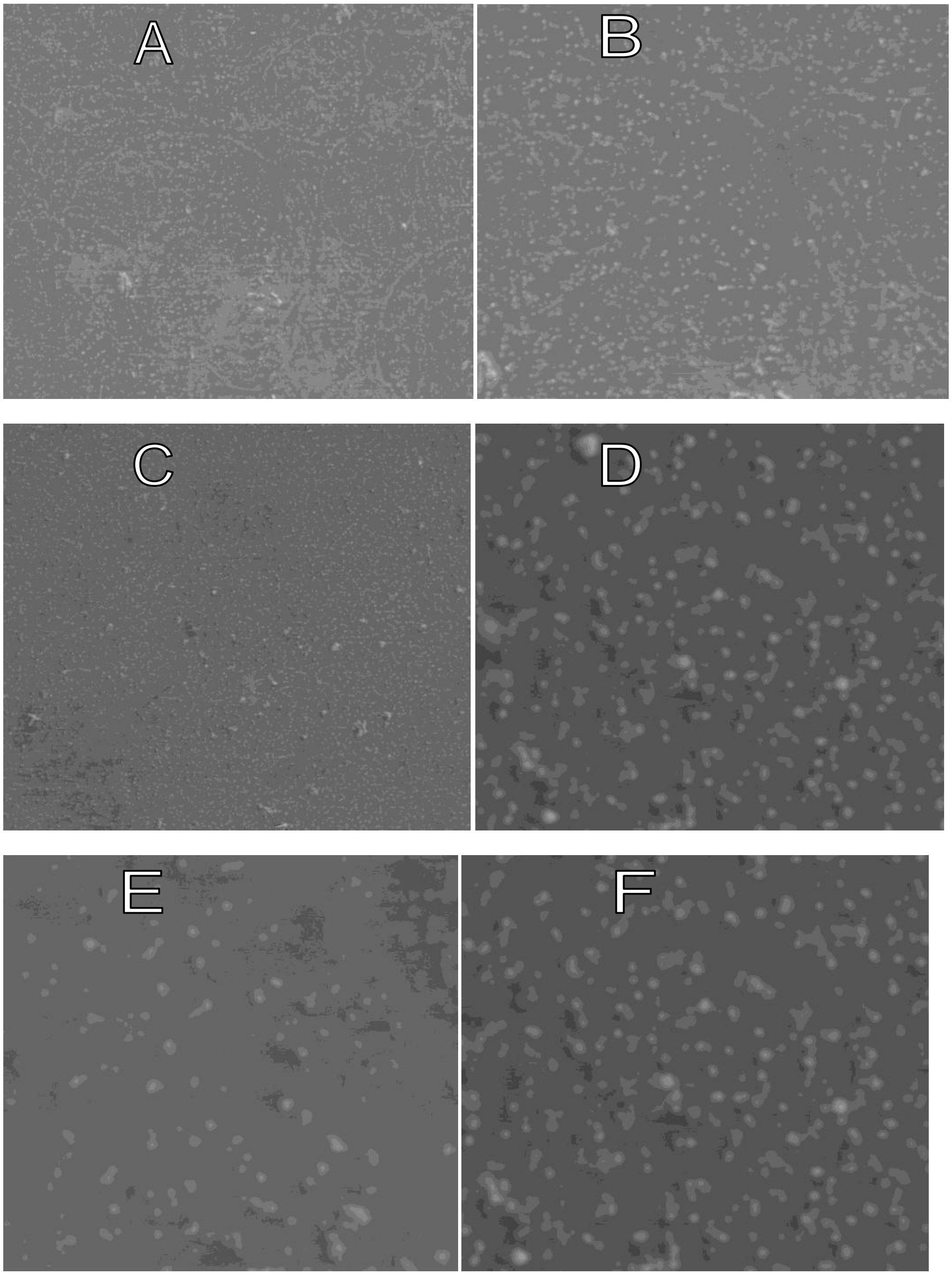

Figure. 3 SEM micrograph of sprayed $CuInS_2$ thin films prepared at different temperature and composition of the solution, A,C & E = 300 ^{0}C and B,D,F = 375 ^{0}C with Cu/In ratio 1.0 (A,B),1.1 (C,D) & 1.2 (E,F) respectively.

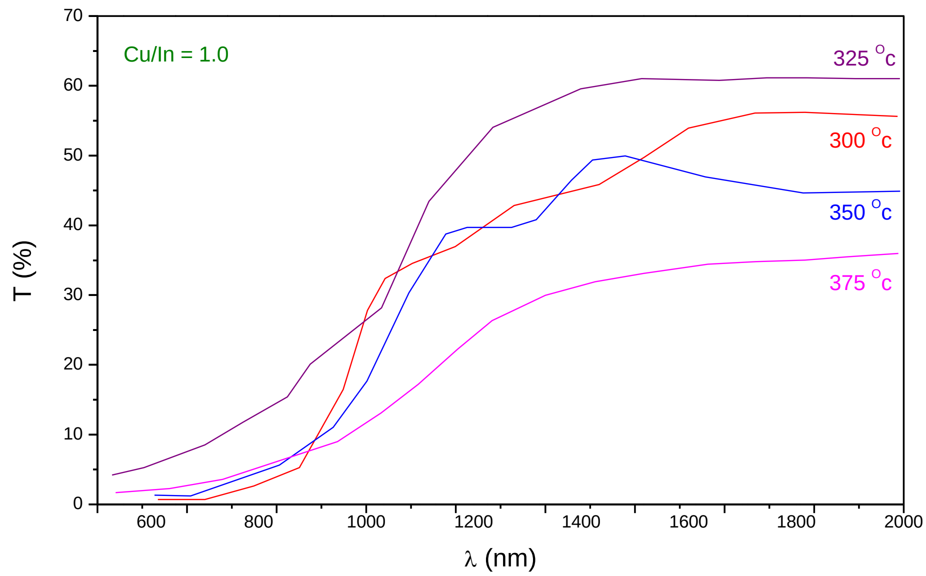

Figure. 4a Optical transmission spectra of sprayed CuInS2 films prepared at different temperatures with Cu/In = 1.0.

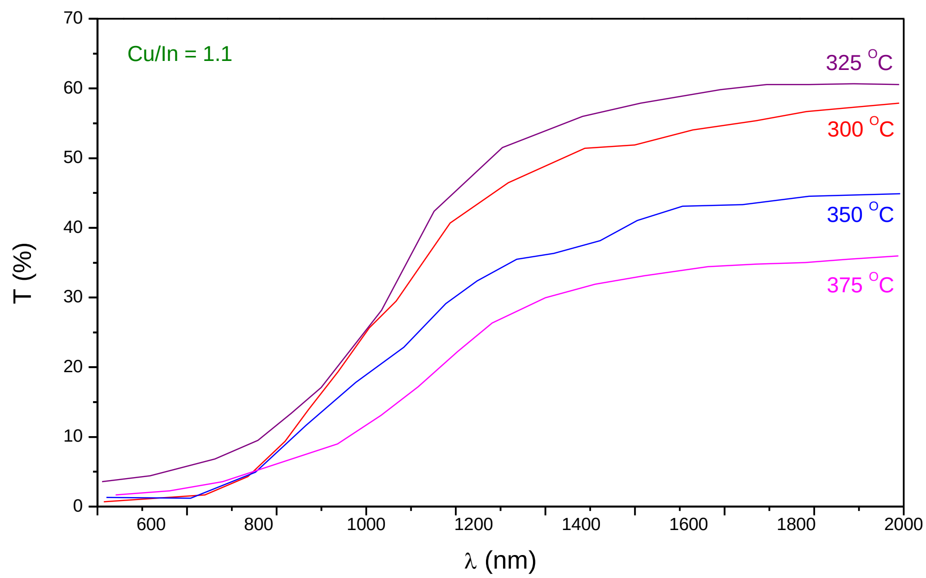

Figure. 4b Optical transmission spectra of sprayed $CuInS_2$ films prepared at different temperatures with Cu/In = 1.1.

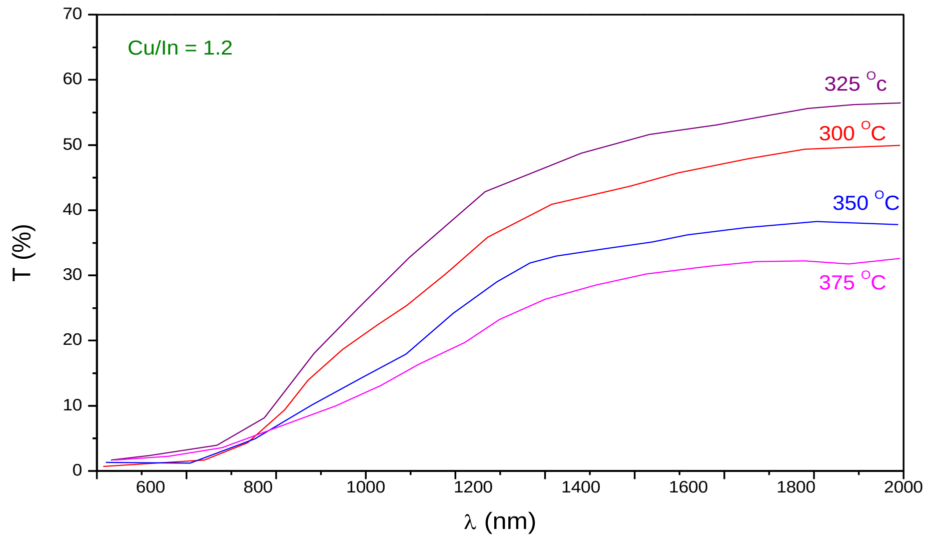

Figure. 4c Optical transmission spectra of sprayed CuInS2 films prepared at different temperatures with Cu/In = 1.2.

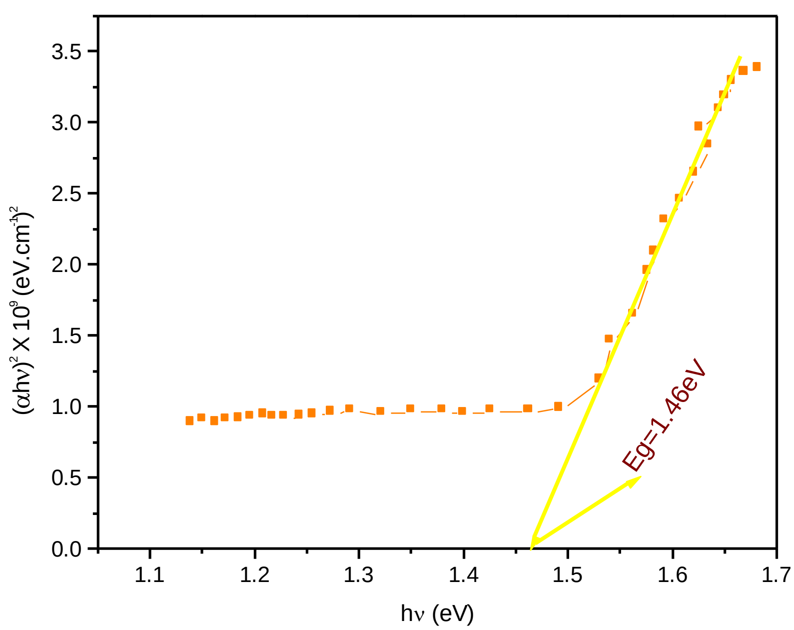

Figure. 5 A plot of (αhυ)² against the photon energy hυ for the films deposited at 350 ⁰C.

Conclusion

The $CuInS_2$ thin films were successfully deposited on glass substrates by spray pyrolysis technique. Results of X-ray diffraction studies showed that a substrate temperature $T_s \cong 350^0C$ for the ratio of concentration in the pulverized solution of [Cu] / [In] = 1.0 permited well crystalline thin films with a preferential orientation along the (112) direction. Scanning electron micrographs of the film showed the evidence of good homogeneity of the films. The deposition temperature had an effect on the resistivity and transmittance behavior. The optical band gap deduced from the plot $(\alpha h\nu)^2$ Vs $h\nu$ by extrapolating straight line from high absorption region was of the order of 1.46 eV and this value was the same order of magnitude with the values given for thin films in the literature.

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Figure Captions

Figure. 1 Schematic representation of the chemical spray pyrolysis setup used for the growth of $CuInS_2$ thin films.

Figure. 2a X-ray diffraction pattern of $CuInS_2$ thin films prepared at different temperature with spraying solution Cu/In = 1.0

Figure. 2b X-ray diffraction pattern of $CuInS_2$ thin films prepared at different temperature with spraying solution Cu/In = 1.1

Figure. 2c X-ray diffraction pattern of $CuInS_2$ thin films prepared at different temperature with spraying solution Cu/In = 1.2

Figure. 3 SEM micrograph of sprayed $CuInS_2$ thin films prepared at different temperature and composition of the solution, A,C & E = 300 ^{0}C and B,D,F = 375 ^{0}C with Cu/In ratio 1.0 (A,B),1.1 (C,D) & 1.2 (E,F) respectively.

Figure. 4a Optical transmission spectra of sprayed CuInS2 films prepared at different temperatures with Cu/In = 1.0.

Figure. 4b Optical transmission spectra of sprayed $CuInS_2$ films prepared at different temperatures with Cu/In = 1.1.

Figure. 4c Optical transmission spectra of sprayed CuInS2 films prepared at different temperatures with Cu/In = 1.2.

Figure. 5 A plot of $(\alpha h\upsilon)^2$ against the photon energy $h\upsilon$ for the films deposited at 350 ^{0}C.

Table captions

Tables 1 Influence of the substrate temperature on the structural and optical properties of $CuInS_2$ film of Cu/In = 1.0

Tables 2 Influence of the substrate temperature on the structural and optical properties of $CuInS_2$ film of Cu/In = 1.1

Tables 3 Influence of the substrate temperature on the structural and optical properties of $CuInS_2$ film of Cu/In = 1.2

Tables 4 Thickness and Refractive Index of $CuInS_2$ film for Cu/In = 1.0

Tables 5 Thickness and Refractive Index of $CuInS_2$ film for Cu/In = 1.1

Tables 6 Thickness and Refractive Index of $CuInS_2$ film for Cu/In = 1.2