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Influence of Spray Deposition Conditions on $CuInS_2$ Semiconductor Properties

[*1]Vijendra A Chaudhari

[*1]Department of Physics, Dayanand Science College, Latur, Maharashtra, India.

Abstract

Spray pyrolysis thin film deposition technique has been used to deposit CuInS2 type semiconductor thin films. The influence of various deposition parameters on the morphology and other properties has been extensively investigated. 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 T_c, pH and Cu/In ion ratio. It is observed that the parameters critical to structural and optical properties of sprayed $CuInS_2$ films are T_c and ion ratio of Cu/In in the spraying solution. Here we report the effect of one of the critical parameter i.e. substrate temperature on the morphological characteristics and optical, electrical properties of the thin films deposited.

Keywords: SEM, structural properties, optical properties, spray pyrolysis.

1. Introduction

Development of thin film solar cells based on $CuInSe_2$ and related alloys have made considerable progress in recent years. $CuInS_2$ is one of the $I\pm III\pm VI_2$ type semiconductors which crystallize in the chalcopyrite structure. Its direct band gap of 1.5 eV, high absorption coefficient and environmental viewpoint that $CuInS_2$ does not contain any toxic constituents makes it suitable for terrestrial photovoltaic applications. 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.

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 [6] 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 [7]. In the present study, the chemical spray pyrolysis (CSP) method is applied to deposit $CuInS_2$ thin films.

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 morphological and optical properties.

2. Experimental

2.1. Experimental Techniques

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 In Cl_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 sulphur 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. The substrate temperature was varied between 300 – 350 ^{0}C. These clean slides were used as substrates for deposition.

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 ($10^0 \leq 2\theta \leq 80^0$) 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 [8]. 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 spectrophotometer "SCHIMADZU" model – UV 160 A. The absorption coefficient α was calculated from transmittance T and reflectance R measurements by using –

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

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 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 chalcopyrite 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. 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.

Tables 1: Influence of the substrate temperature of $CuInS_2$ film of Cu/In = 1.0

T_s (^{O}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

Tables 2: Influence of the substrate temperature of $CuInS_2$ film of Cu/In = 1.1

T_s (^{O}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 3: Influence of the substrate temperature of $CuInS_2$ film of Cu/In = 1.2

T_s (^{O}C)	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 1 shows the typical scanning electron micrograph of $CuInS_2$ thin films. Fig. 1 A,C,E (300 ^{0}C) & Fig. 1 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 ^{O}C showed crystallites with sizes in the range 40-80 nm (Fig. 1 A,C,E) while the films grown at 375 ^{O}C consisted of sharp-edged crystallites with sizes of 50-200 nm (Fig. 1 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 ^{O}C (Cu/In = 1:1) showed the formation of separate crystals on the film surface (Fig. 1 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.

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

Substrate Temp (^{O}c)	Thickness (Å)	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 = 1.2

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

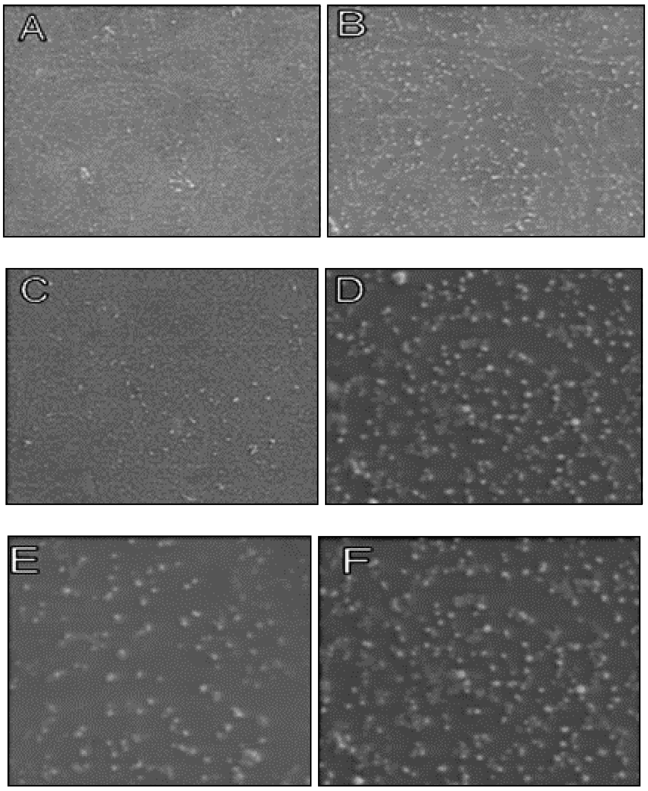

Fig 1: SEM micrograph of sprayed $CuInS_2$ thin films prepared at A,C & E = 300 ^{O}C and B,D,F = 375 ^{O}C with Cu/In ratio 1.0 (A,B),1.1 (C,D) & 1.2 (E,F) respectively.

Absorption coefficient and band gap values for spray $CuInS_2$ thin films were determined from the optical transmission data. Figures 2 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 ^{O}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

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

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 3. The band gap Eg = 1.46 eV was obtained from extrapolated intercept with the hν axis and tabulated in Table 1, 2 & 3.

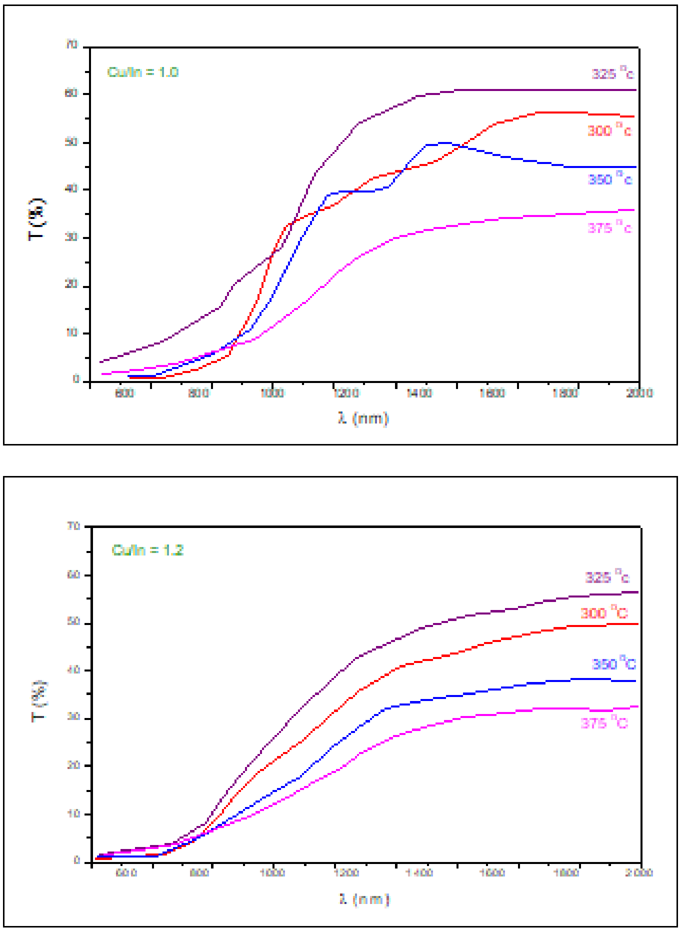

Fig 2: Optical transmission spectra of sprayed CuInS2 films prepared at different temperatures with Cu/In = 1.0 and 1.2.

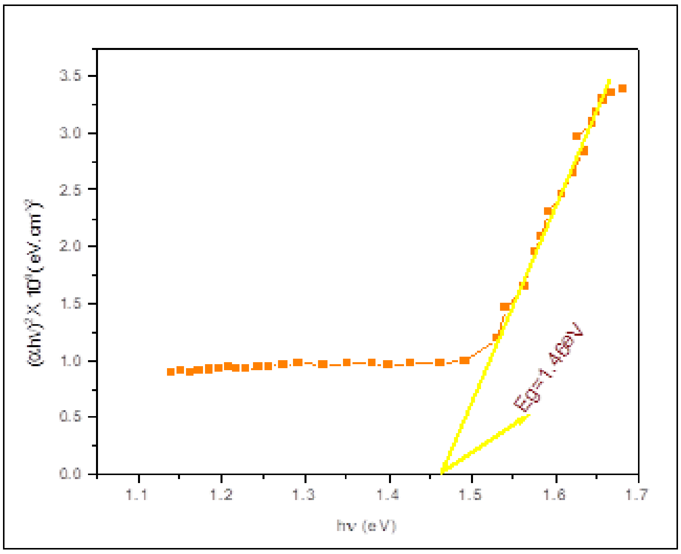

Fig 3: A plot of $(\alpha h\upsilon)^2$ against the photon energy hυ for the films deposited at 350 ^{O}C.

Conclusion

The spray pyrolysis method was applied to deposit $CuInS_2$ thin films on glass substrates. The parameters which are critical to the formation of single phase crystalline films were studied symmetrically and optimized. The dependent of structural and morphological properties of the spared films on the preparation conditions such as substrate temperature and ion ratio of Cu/In in spraying solution have been carried out to achieve optimum conversion efficiency. The optical band gap deduced from the plot $(\alpha h\nu)^2$ Vs hν by extrapolating straight line from high absorption region was of the order of 1.46 eV.

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