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Structural, Optical and Morphological Properties of Sprayed $CuInS_2$ (CIS) films for solar cells

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Abstract

$CuInS_2$, (CIS) is the suitable material for solar cell application due to its bandgap and optical absorption properties. The CIS films were deposited on thoroughly cleaned soda lime glass (SLG) substrates at 450 ℃ with different morality ratios of copper, indium and sulfur by using home-built spray pyrolysis technique. The resultant films were characterized by using X-ray Diffraction, UV-visible spectroscopy, scanning electron microscopy and surface profilometer. The X-ray diffraction study of as-prepared films showed the tetragonal CIS phase. The data for lattice parameters a and c for all films is found to be matching with the standard reported data for tetragonal CIS. The values for crystallite size of CIS films are in nanometric range indicating thereby nano-crystalline nature of the all CIS films. The SEM study showed particles to be nearly in spherical shape and each spherical particle is almost soft agglomerate and contains number of primary spherical shaped particles. Qualitatively, all the CIS films are dense and the average particle size is found to be in nanometric range which supports the XRD results. The EDAX spectra for all the CIS films showed the presence of peaks corresponding to the Cu, In and S only confirming thereby the material purity of all CIS films. The absorbance spectrum showed the sharp increase in absorption at the wavelength near to the absorption edge of the threshold wavelength. The values for optical band gap obtained from Tauc's plots are in range of 1.03 - 1.13 eV. The thickness values of CIS films are found to be in range of 205 to 224 nm.

Keywords: $CuInS_2$, film; Spray pyrolysis; Optical properies; X-Ray diffraction.

Introduction

With the rapid depletion of conventional sources of energy, the sun offers an inexhaustible energy. The question is that can we trap this energy? Photovoltaic conversion of solar energy into electrical energy offers an attractive alternative for generation of electrical alternative. Photovoltaic devices called solar cells have long been used to power the satellites. However, the cost of these has been high for their terrestrial applications. The cost has come down substantially during last two decade but it has to be further reduced to existing energy systems. To reduce the costs further, efficiency of PV cells must be increased and the manufacturing costs will have to be decreased. At present, module efficiencies are as high as 15 %. The main constraint on the efficiency of a solar cell is related to the band gap of the semiconductor material of a PV cell. A photon of light with energy equal to or greater than the band gap of the material is able to free-up one electron when absorbed into the material. However, the photons that have energy less than the band gap are not useful for this process, because when absorbed on the cell, they just produce heat. For the photons with more energy than the band gap, the excess energy above the band gap is not useful in generating electricity. The excess energy also simply heats up the cell. These reasons account for a theoretical maximum limit on the efficiency of a conventional single-junction PV cell to less than 25 %.

Thin-film technology has a great potential for cost reduction. Thin film is a material created by the random nucleation and growth processes of individually condensing / reacting atomic / ionic /molecular species on a substrate. The structural, chemical, metallurgical and physical properties of such material are strongly dependent on a large number of deposition parameters and may also be thickness dependent. Thin films may encompass a considerable thickness range, varying from a few nanometers to tens of micrometers and thus are best defined in terms of the production processes rather than by thickness following features of thin-film processes have been shown to be of interest for PV technologies. The thin film PV is also characterized by flexibility to deposition by several techniques and several possible materials. One of the important features of thin film PV is the low requirement of the material, due to the high absorption coefficient in the energy region of interest.

Copper indium disulfide, $CuInS_2$ (CIS) is a chalcopyrite material belonging to the group of ternary semiconductors with molecular formula ABX2. The system of copper chalcopyrite includes a wide range of band gap energies (E_g) from 1.04 eV (for $CuInSe_2$) up to 2.7 eV (for $CuAlS_2$), covering most parts of the visible spectrum [1]. This along with the wide range of carrier mobility offered by these semiconductors has resulted in their applications in photovoltaic, light emitting diodes and non linear optical devices. The crystal structure of ternary chalcopyrite has eight atoms per unit cell and can be considered as a superlattice of zincblende structure. Each anion is tetrahedrally coordinated to two atoms of both cations, while each cation is coordinated to four anions. $CuInS_2$ (E_g = 1.5 eV) has nearly optimum band gap for energy conversion, large absorption coefficient and good stability for solar radiation [2]. The higher band gap favors the device response at higher temperatures and improves blue response of the cell. Large number of possible intrinsic defects and tolerance of this material to off stoichiometries make it all the more interesting. Important progresses in understanding the properties of $CuInS_2$ have been made during the last few decades, though a lot of questions still remain unanswered [3].

$CuInS_2$ (CIS) has the potential to reach high conversion efficiency due to its large absorption coefficient and direct band gap of 1.5 eV, and will match well with the solar spectrum. $CuInS_2$ (CIS) films have been prepared using various techniques including single-and double-source evaporation, flash evaporation, R.F. sputtering, chemical vapour deposition, and spray pyrolysis technique. The physical properties of $CuInS_2$, such as the band gap and the optical absorption of photons in the solar spectrum wavelength range are known to be appropriate for the fabrication of thin films solar cell. Therefore, this material has been used to make solar cells.

In the present work, the spray pyrolysis method was used to produce $CuInS_2$ (CIS) thin films. The spray pyrolysis is an attractive method for large area thin film production because it is of low-cost and easy to make process. The aim of this work is to produce $CuInS_2$ (CIS) thin films by means of the spray pyrolysis technique and investigate their structural, optical, and morphological properties for solar cell applications.

Experimental Work

The Copper Indium Sulfide, $CuInS_2$ (CIS) films were deposited on thoroughly cleaned soda lime glass (SLG) substrates by using home-built spray pyrolysis technique. The soda lime glass (SLG) substrates were used for the deposition of films. The SLG substrates were thoroughly cleaned by using the procedure as given below.

Cleaning of SLG substrates

i. Initially, SLG substrates were washed with laboline detergent and then rinsed with double distilled water (DDW).
ii. In second step, substrates were heated in concentrated chromic acid (0.5 M) for 1 hr and then kept in it for 12 hr.
iii. After chromic acid treatment, the substrates were rinsed and cleaned ultrasonically in DDW for 20 min.
iv. Finally, the substrates were ultrasonically cleaned in AR grade acetone for 10 min. and then dried under IR lamp.

The thoroughly cleaned SLG substrates were then subjected immediately for deposition of different films.

Depositions of CIS films

Table 1 shows the AR grade precursor materials (Thomas Baker Chem.) used in the present work of deposition of CIS films by using spray pyrolysis method [4 - 11]. All the chemicals of AR grade were used as received without further any purification. The precursor solutions were prepared in double distilled water (DDW). For the equimolar preparation, the 0.05 M solution of $CuCl_2\ 2H_2O$, $InCl_3\ 3H_2O$ and NH_2CSNH_2 were prepared in DDW. All these solutions were mixed together ultrasonically for 30 min. The CIS films were deposited on thoroughly cleaned SLG substrates by using process parameters: (i) spray gun nozzle - substrate distance = 30 cm, (ii) carrier gas (compressed air) flow rate = 20 lpm, (iii) deposition time = 5 min., (iv) solution flow rate = 6 ml/min. and (v) substrate temperature (T_s) = 450 ^{0}C. After each deposition, the films were cooled naturally to the room temperature (RT).

Table 1. Materials and their molarities used for depositions of CIS films

Parameter	Precursor		
	Copper	Indium	Thiourea
Formula	$CuCl_2$ $2H_2O$	$InCl_3$ $3H_2O$	NH_2CS NH_2
Molecular weight (gm)	170.48	276.18	76.12
	Molarity (M)		
Equimolar	0.05	0.05	0.05
Indium deficient	0.05	0.025	0.05
Indium rich	0.05	0.075	0.05

By using the above mentioned procedure CIS were also prepared with indium deficient and indium rich spray solutions. The crystallization of CIS films takes place via. following reaction,

$$CuCL_2 + InCl_3 + 4CS(NH_2)_2 + 8H_2O \rightarrow CuInS_2 + 5NH_4Cl + 4CO_2 + 2H_2S + 3NH_3 \quad \text{--- (1)}$$

The volatile components released during the reaction are removed outside by using the exhaust unit. The $CuInS_2$ films deposited on the surface of glass substrate under controlled conditions. The CIS films deposited at equimolar, indium deficient and indium rich spray solutions are identified as 1, 2 and 3 respectively. The resultant as-prepared films were characterized by using different physical techniques. X-ray diffraction patterns were recorded by using Bruker D8 Advance (filtered CuK_α radiation, λ = 1.5406 Å) machine. Thickness of the films was measured by using surface profiler (KLA Tencor P -16+). The optical spectra of resultant films were recorded by using the UV-Visible spectrophotometer (V-670, JASCO UV-VIS-NIR spectrometer). Surface morphology study and elemental analysis were done by using scanning electron microscope (JEOL JSM-6360-LA and Philips XL - 30) and energy dispersive analysis of X-rays respectively.

Results and Discussion

The spray pyrolysed CIS films were characterized by using X-ray Diffraction, UV-visible, Scanning Electron Microscopy and surface profilometer for further analysis.

X-Ray Diffraction Studies

All $CuInS_2$ films prepared at different molar ratios of precursor solutions by using spray pyrolysis parameters as mentioned in experimental section are found to be non-scratchable, well adherent and uniformly thick qualitatively. Figure 1 shows the X-ray diffraction patterns (XRD) of spray pyrolyzed 1, 2 and 3 CIS films**.**

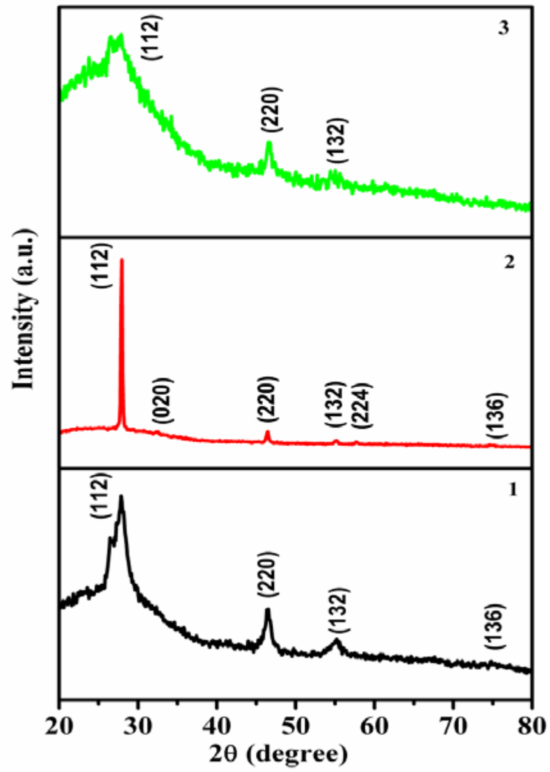

Figure 1. XRD patterns of 1, 2 and 3 CIS films

With reference to the JCPDF data file no. 47- 1372, the X-ray diffraction studies of as-prepared CIS films show the crystallization of $CuInS_2$ films with tetragonal symmetry. By using Bragg's diffraction condition (equation 2) the 'd' values are calculated for different planes.

$$2d\sin\theta = n\lambda \quad \text{--- (2)}$$

where, d = interplanar spacing, θ = angle of diffraction, n = order of diffraction and λ = 1.54 Å (wavelength of X-rays). Table 2 gives the data for observed 'd' values of three planes for the as-prepared CIS films and standard 'd' values from PCPDF file no.: 47-1372 for tetragonal $CuInS_2$ phase.

Table 2. Data for observed d values for as-prepared CIS films

hkl plane	Standard* 'd' (Å) value	Observed d (Å) values for different CIS films		
		1	2	3
112	3.1950	3.2052	3.1940	3.2052
220	1.9520	1.9506	1.9546	1.9506
132	1.6654	1.6620	1.6620	1.6675

[* - PCPDF file no.: 47-1372]

In this case, the observed 'd' values are found to be matching with standard 'd' values indicating thereby the formation of single CIS phase with tetragonal symmetry in all as-prepared CIS films [4 - 5]. From Figure 1, it is clear that the diffraction intensity of (112) plane is highest as compared to the other planes. This indicates the preferred orientation of all the as-prepared CIS films along [112] direction.

The d-spacing relation (equation 3) for tetragonal symmetry is used to obtain the values of lattice parameters: a and c for different as-prepared CIS films.

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

Table 3 gives the values of lattice parameters 'a' and 'c' calculated by using d-spacing equation for as-prepared CIS films. It observed that, the calculated values lattice parameters are found to be perfect matching with standard values: a = 5.5202 Å and c = 11.122 Å given in PCPDF data file no.: 47-1372 for tetragonal CIS phase.

The values for crystallite size are calculated for as-prepared CIS films by using Scherrer formula (equation 4).

$$d = \frac{0.9\lambda}{\beta \cos\theta} \quad \text{--- (4)}$$

where, $\lambda = 1.54 \times 10^{-10}$ m, β = full width at half maximum (fwhm) and θ = Bragg's angle for the stronger (112) reflection.

Table 3. Data for lattice parameters for as-prepared CIS films

hkl plane	Lattice parameter (Å)	As -prepared CIS film		
		1	2	3
112	a	5.5471	5.425	5.5470
	c	11.2328	10.746	11.2328
220	a	5.5172	5.5318	5.5172
	c			
132	a	5.5076	5.5105	5.5278
	c	10.8689	10.868	10.9272

The values for crystallite size obtained for 1, 2 and 3 as-prepared CIS films are found to be 24, 49, and 15 nm respectively. The data for crystallite sizes is found to be in nanometric range. This clearly indicated the nano-crystalline nature of the CIS films deposited at substrate temperatures (T_s) 450 ^oC.

Scanning Electron Microscopy Studies

Figure 2 gives the scanning electron microscope (SEM) images for the 1, 2, and 3 as-prepared CIS films. Following general observations are noted from the SEM images.

i. The particles are observed to be nearly in spherical shape for all the films.

ii. Each spherical particle is almost soft agglomerate and contains number of primary spherical shaped particles [6-7].

The morphological characterization studies showed nearly spherical morphology of particles with ~ mono-sized distribution of particles. The average particle size is found to be in nanometric range. Qualitatively, all the CIS films are dense.

Energy Dispersive X-ray Analysis

Figure 3 gives the energy dispersive X-ray (EDAX) analysis spectrum for a typical as-prepared CIS film no. 2.

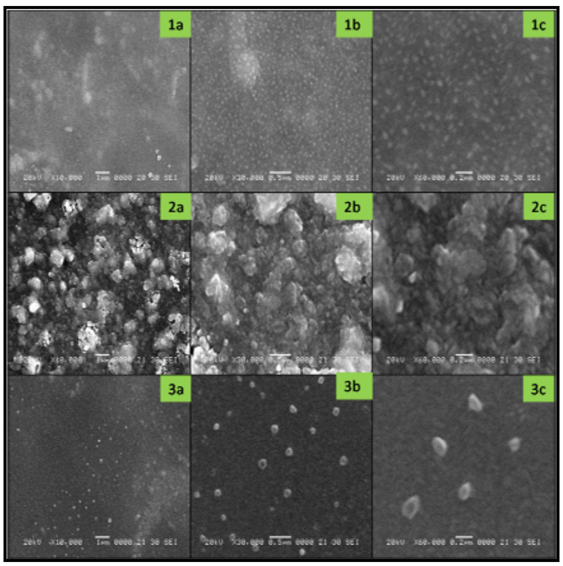

Figure 2. SEM images for 1, 2 and 3 as-prepared CIS films at three different magnifications.

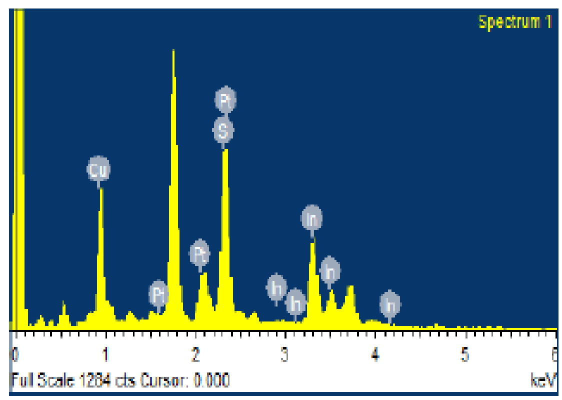

Figure 3 EDAX spectrum for the as-prepared CIS film no. 2

It shows the presence of peaks corresponding to only Cu, In and S in as-prepared CIS film. This confirms the purity of material of as-prepared tetragonal CIS films generated in the present work [4, 8 - 9]. The EDAX data for weight % and atomic % of various elements in as-prepared CIS film no. 2 is given in Table 4. The EDAX data clearly indicates the indium (In) deficiency in the as-prepared CIS film no. 2.

Table 4. EDAX data CIS film no. 2.

Parameter	Element		
	Cu	In	S
Weight %	31.03	40.92	28.05
Atomic %	28.40	20.73	50.83

UV-Visible Spectroscopy Studies

Optical absorbance curves for as-prepared 1, 2 and 3 CIS films are shown in Figure 4. Optical absorbance against the wavelength is recorded for CIS films in the wavelength range 200 - 1200 nm with glass as the reference. The absorbance spectra show the sharp increase in absorption at the wavelength near to the absorption edge of the threshold wavelength. The energy corresponding to this wavelength determines the band gap of as-prepared CIS film. The values for optical band gap are obtained from Tauc's plots generated by using the relation,

$$(\alpha h\nu)^2 = (h\nu - E_g) \quad \text{--- (5)}$$

where, absorption coefficient α is given by,

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \quad \text{--- (6)}$$

where, t = film thickness and T = % transmission of the film. The nature of optical transition in as-prepared CIS film is direct. The Tauc plots generated by using the equation (5) are given in Figure 4 (inset). It shows the variation of $(\alpha h\nu)^2$ versus hν for as-prepared CIS films. The extrapolation of straight-line portion of a plot to zero absorption edge (intercept on X-axis) gives the value of band gap energy (E_g). The values of direct band gap energies are found to be 1.03, 1.08 and 1.13 for the as-prepared 1, 2 and 3 CIS films respectively. These values of E_g are found be close to the standard value reported for CIS films [9 - 11].

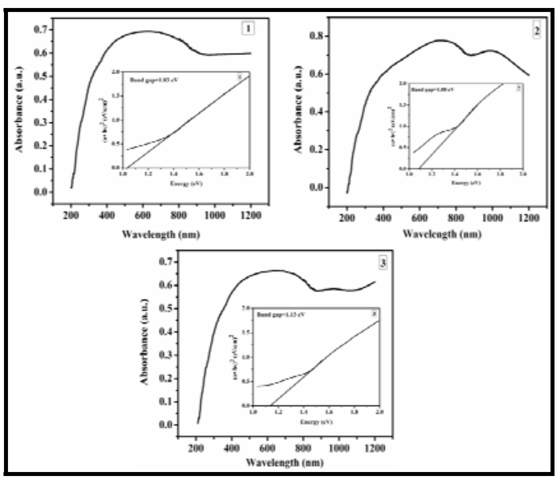

Figure 4. Optical absorbance vs. wavelength and respective Tauc plots (inset figure) for 1, 2 and 3 as-prepared CIS films

Surface Profilometer Studies

The surface profilometer was used for the measurement of thicknesses of as-prepared CIS films. The values of thickness of as-prepared 1, 2 and 3 CIS films are found to be 217, 205 and 224 nm respectively. As an absorber layer, the thickness in range of 2 - 4 µm is required. Hence, these observed values of thickness are too small to absorb the radiation.

Conclusions

The spray pyrolysis is cheap and easy technique to prepare the $CuInS_2$ films. The ratio of precursor solutions is having profound effect on the crystallization of $CuInS_2$ film. The films prepared with indium deficient precursor solution showed the better crystallization as compared to the film prepared with precursor solution having equimolarity and indium richness. The $CuInS_2$ films prepared at 450 ^{0}C substrate temperature by using spray pyrolysis technique are non-scratchable, well adherent, uniformly thick, nanocrystalline, pure and single phase with tetragonal symmetry.

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