Materials Science-Poland, 31(2), 2013, pp. 193-200
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.2478/s13536-012-0094-0

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Optimization of deposition temperature of SILAR Cu-rich $CuInS_2$ thin films

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$CuInS_2$ (CIS) is studied widely as a promising absorber material for high efficient and low cost thin film solar cells. CIS thin films are prepared on soda lime glass substrates using Successive Ionic Layer Adsorption and Reaction (SILAR) technique at different deposition temperatures (40 to 70 °C). The structural, compositional and optical properties are studied with x-ray diffractometer, energy dispersive x-ray analyzer and spectrophotometer. The influence of the deposition temperature on the properties of CIS thin films is discussed in this paper in detail.

Keywords: *$CuInS_2$; SILAR; XRD; EDAX; UV-spectrophotometer*

1. Introduction

Photovoltaic devices are most suitable for the production of convenient and low-cost energy but a major problem is the development of easily available and ecofriendly absorbers that can give reasonable high-efficiency cells [1]. Currently, chalcopyrite semiconductors are being investigated as one of the most promising candidates for absorber layers in thin film solar cells. The ternary compound $CuInS_2$ is attractive because of its large band gap energy (E_g = 1.5 eV) raising the potential for high open circuit voltages [2]. The large band gap is also advantageous for a large-area monolithic module because of its low series resistance loss [3]. $CuInS_2$ has excellent properties such as high absorption coefficient (of about 10^5 cm^{-1}), an exceptional insensitivity to radiation damage or impurity and environmental friendly nature *etc.* [4]. $CuInS_2$ offers an easy upscaling and low production costs [5]. Theoretically calculated efficiency ranges between 27 and 32 % for $CuInS_2$ based homojunctions. The difference between the theoretical efficiency and the measured efficiency (of about 9.5 %) [1] is attributed to the defect chemistry of the films [6].

A variety of techniques such as spray pyrolysis [7–9], ionic layer gas reaction [10], sputtering [11, 12], liquid-liquid interface reaction technique [13], electron beam evaporation [14], chemical deposition [15] and molecular beam epitaxy [16], have been employed to deposit $CuInS_2$ thin films. In this study, Cu-rich CIS thin films have been prepared at five different deposition temperatures (40, 50, 60, 65 and 70 °C) by SILAR technique as it is simple, attractive, low cost and less time consuming. Moreover, an attempt has also been made to study the influence of deposition temperature on the structural, compositional and optical properties of Cu-rich CIS films and the results are discussed and reported in this paper.

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2. Experimental details

2.1. Film preparation

$CuSO_4$ (12.5 ml, 0.1 M) and $InCl_3$ (12.5 ml, 0.2 M) were taken and mixed in a 100 ml beaker and the pH of the solution was adjusted to 5 with triethanolamine and hydrazine hydrate (TEA+HH), which promoted Cu-In formation [17]. The reaction mixture was stirred well so that a clear homogeneous solution was formed (cationic solution). CH_4N_2S (25 ml, 0.5 M) was taken in another beaker (anionic solution) and its pH was adjusted to 12 by the addition of ammonia. A digital pH meter (ELICO LI-120) was used to adjust the pH of the reaction mixture. The pH meter was standardized using buffer solutions of pH 4+0.05 and 9.2+0.05. The deposition was carried out with a SILAR coating unit HO-TH-03A at five different temperatures (40, 50, 60, 65 and 70 °C).

Well-cleaned soda lime glass substrate was immersed in the mixed cationic precursors ($CuSO_4$+$InCl_3$) for 30 sec so that Cu and In ions were adsorbed (diffusion, reaction and adsorption) on the substrate surface. The substrate was rinsed with ion-exchange water for 30 sec to remove the unattached ions (convection, diffusion and desorption). The substrate with pre-adsorbed Cu and In ions reacted with the newly adsorbed sulphur from the anionic solution (diffusion, reaction and adsorption) to form $CuInS_2$. The substrate was then rinsed with ion exchange water for 30 sec to remove the loosely bounded particles (convection, diffusion and desorption).

The number of deposition cycles was varied to obtain thin films of different thicknesses (by gravimetric technique, after annealing the films at 100 °C for 60 min). As peeling off the CIS thin films occurred due to dissociation mechanism after 50 deposition cycles [17], the number of the deposition cycles was optimized as 50.

2.2. Growth mechanism

Thiourea dissolved in water and formed H_2S in the anionic solution, as per Equation (1). Cu^{2+} and In^{3+} ions, due to immersion in cationic solution ($CuSO_4$+$InCl_3$), react on the substrate with the S^{2-} ions of H_2S and form the compounds of CuS and In_2S_3, according to Equations (2) and (3). By repeating the above cycles, CuS and In_2S_3 react to form $CuInS_2$ as per Equation (4) [18].

$$CS(NH_2)_2 + 2H_2O \rightarrow 2NH_3 + H_2S + CO_2 \quad (1)$$

$$CuSO_4 + H_2S \rightarrow CuS + H_2SO_4 \quad (2)$$

$$2InCl_3 + 3H_2S \rightarrow In_2S_3 + 6HCl \quad (3)$$

$$CuS + In_2S_3 \rightarrow 2CuInS_2 + S \quad (4)$$

2.3. Film characterization

X-ray diffraction was used to identify the crystalline phases, using SHIMADZU (Model 6000) diffractometer with CuKα (λ = 1.5418 Å) radiation in 2Θ range 20 to 80°. The atomic composition was determined by energy dispersive x-ray analyzer (EDAX) with a INCA penta FET X3 7582. The optical transmission spectra of the prepared thin films were taken using JASCO-UV/VIS/NIR (JASCO V-570) optical spectrophotometer in the wavelength range of 200 – 2500 nm.

3. Results and discussion

3.1. Structural analysis of SILAR Cu-rich CIS thin films

Fig. 1 shows the x-ray diffraction profiles of $CuInS_2$ thin films prepared at different temperatures. The observed peaks (Fig. 1) and the estimated lattice constants (Table 1) are in agreement with JCPDS file (27-0159) of $CuInS_2$ and hence, the prepared films are $CuInS_2$ with tetragonal structure. The splitting of (204/220) peak in the x-ray diffraction profile of the films is a characteristic sign of tetragonal chalcopyrite structure as reported by He *et al.* [19]. Cu_2S phase exists in the CIS films prepared at 40 °C and 65 °C. The existence of secondary phase proves the incomplete reaction of CuS with In_2S_3 to form CIS film [20]. The crystalline orientation (112) is absent in the $CuInS_2$ films prepared at 70 °C. It has been reported that solar cells with decreased series resistance may be obtained from $CuInS_2$ absorbers with a (112) crystalline orientation [21]. The presence of Cu_2S and the absence of (112) orientation suggest that the deposition temperatures of 40 °C 65 °C and 70 °C are not preferable for the preparation of $CuInS_2$ thin films. The absence of secondary phase in the films prepared at 50 °C and 60 °C confirms the complete formation of CIS films. The orientation factors of (220/204) and (112) planes of $CuInS_2$ films prepared at 50 °C and 60 °C are presented in Table 2. It has been identified that the CIS films prepared at 50 °C as well as 60 °C have (112) preferential orientation due to the higher orientation factor of (112) plane than that of (220/204) plane. $CuInS_2$ films prepared at 60 °C have slightly higher orientation factor (0.68) than the film prepared at 50 °C (0.67). The crystallite size was calculated by the x-ray line broadening method using the

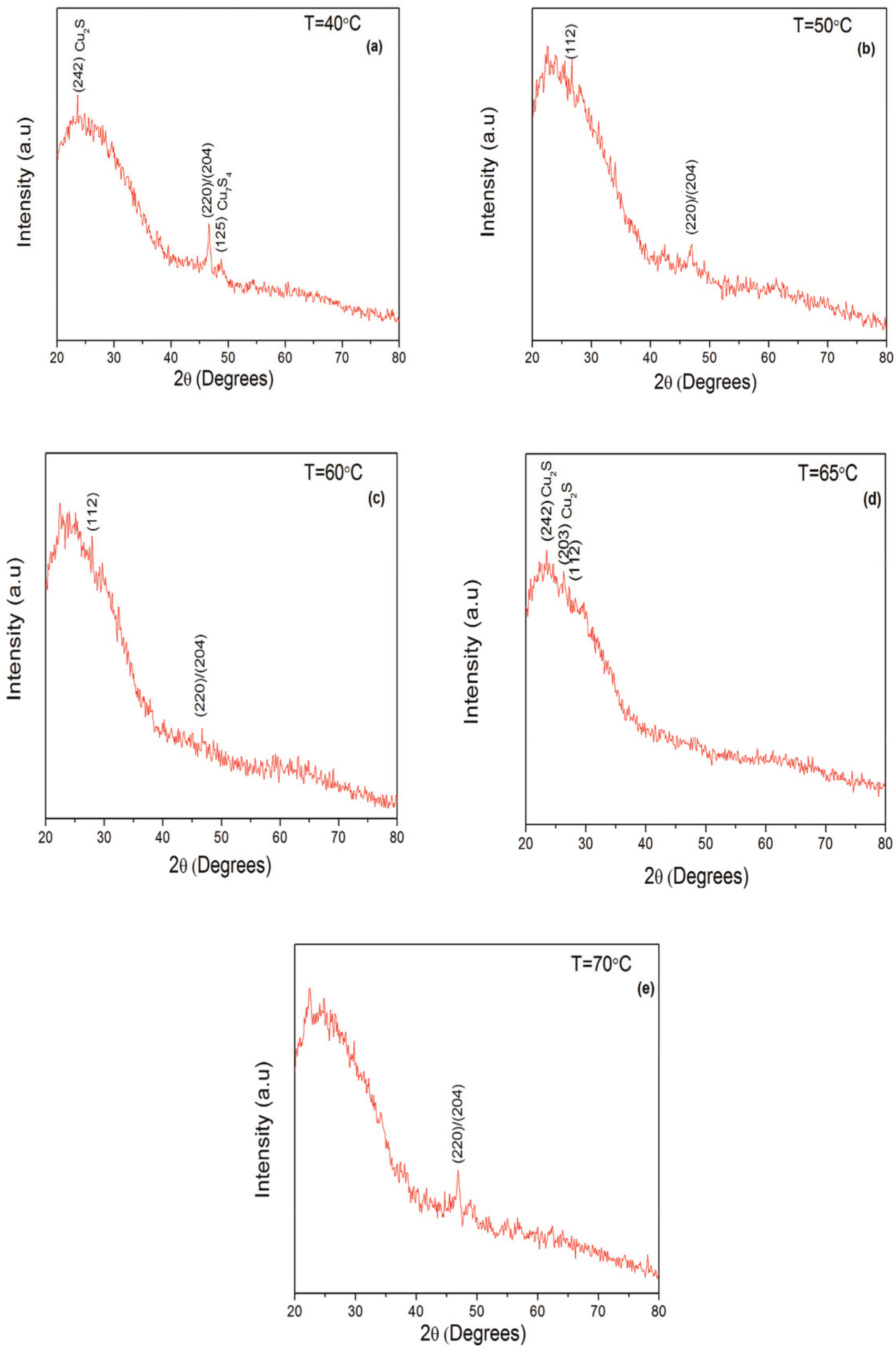


Fig. 1. XRD profiles of CIS thin films prepared at different deposition temperatures.

Table 1. Structural parameters of CIS thin films.

Deposition temperature (°C)	Lattice constant (Å) a (JCPDS: 5.522)	Lattice constant (Å) c (JCPDS: 11.133)	Axial ratio (c/a)	Tetragonal distortion (2-c/a)	Crystalline size D_c (nm)	Dislocation density ($\times 10^{15}$ lines/m^2)	Number of crystallites per unit area ($\times 10^{14}$m^{-2})	Strain ($\times 10^{-3}$)
40	5.508	11.135	2.02	-0.020	12	6.6	3730	3.0
50	5.440	11.163	2.05	-0.050	10	10.2	1500	3.8
60	5.399	11.231	2.08	-0.080	**84**	**0.1**	2	**0.4**
65	5.538	11.056	1.99	0.003	14	5.3	415	2.7
70	5.481	11.673	2.12	-0.120	12	7.4	1300	3.2

Table 2. Confirmation of preferential orientation.

Plane	Orientation factor of the plane at different temperatures 50 °C	60 °C	Preferential orientation
(112)	0.67	**0.68**	**(112)**
(220/204)	0.33	0.32	

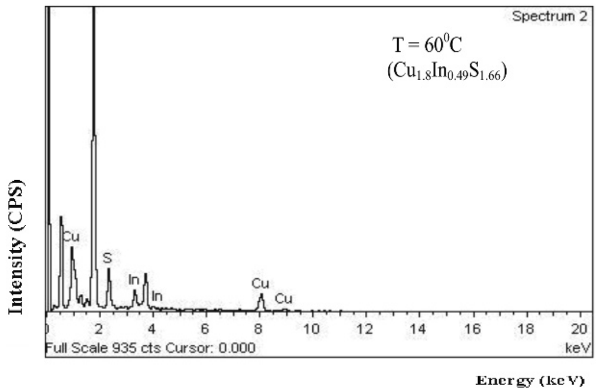


Fig. 2. Representative EDAX spectra of Cu-rich CIS thin film.

Scherrer formula and the other structural parameters such as dislocation density, number of crystallites per unit area and strain were estimated and are presented in Table 1 [22]. CIS films prepared at 60 °C have a (112) preferred orientation, larger crystalline size and less defects such as dislocation density and strain, compared to the films prepared at other temperatures. More detailed investigation, comprising compositional and optical analysis, was carried out for all the samples, including the samples prepared below 50 °C and above 60 °C, for two reasons: (i) to support XRD results and also (ii) to confirm that 60 °C is the optimum deposition temperature for preparing SILAR Cu-rich $CuInS_2$ thin films.

3.2. Compositional analysis of SILAR Cu-rich CIS films

Fig. 2 shows the representative energy dispersive x-ray spectra of $CuInS_2$ thin film prepared at 60 °C. EADX analysis confirms the presence of copper, indium and sulphur in the deposited film with non-stoichiometric nature. The peak at 1.75 keV shows the presence of silicon which is attributed to the glass substrate. The absence of other peaks in the EDAX spectra indicates that the prepared CIS thin films are pure in nature without impurities. From the atomic percentage of copper, indium and sulphur it can be concluded that the crystals contain copper and sulphur with small quantity of indium on the surface. The strong deviation of the surface composition from the stoichiometry has been found and the films are identified as Cu-rich $CuInS_2$.

It is interesting to note that the lattice constants can be estimated by substituting the composition of sulphur (x) in the equation: $a = 5.769 - 0.253x$ and $c = 11.726 - 0.669x$ [23] and are presented in Table 3. They are in good agreement with JCPDS values (JCPDS No.27-0159).

The electrical properties of the semiconductor are determined by the compositional deviations from the ideal chemical formula of the $CuInS_2$ compound, which can be described conveniently by two parameters, non-molecularity (Δx) and non-stoichiometry (Δy) [10]. The variation of Δx would lead to the formation of equal numbers of donors and acceptors. The estimated Δx value varies from

Table 3. Parameters estimated from EDAX spectra of CIS films.

Deposition temperature (°C)	Composition	Cu/In	Lattice constant (Å) a (JCPDS: 5.522)	Lattice constant (Å) c (JCPDS: 11.133)	Axial ratio (c/a)	Tetragonal distortion (2-c/a)	Non-mole-cularity parameter (Δx)	Non-stoi-chiometery parameter (Δy)	Type of conduction
40	$Cu_{2.3}In_{0.18}S_{1.44}$	12.8	5.444	10.762	1.97	0.02	11.8	0.01	
50	$Cu_{2.2}In_{0.22}S_{1.47}$	10.0	5.437	10.742	1.97	0.02	9.0	0.02	
60	$Cu_{1.8}In_{0.49}S_{1.66}$	3.70	5.395	10.615	1.96	0.03	2.7	0.01	p
65	$Cu_{1.8}In_{0.47}S_{1.69}$	3.80	5.388	10.595	1.96	0.03	2.8	0.05	
70	$Cu_{2.05}In_{0.38}S_{1.56}$	5.40	5.413	10.668	1.97	0.02	6.1	0.02	

2.7 to 11.8 which in turn results in a compensated crystal (Table 3). The parameter is related to the electronic defects and could determine the type of the majority charge carriers. Films with $\Delta y > 0$ would behave as p-type material while the ones with $\Delta y < 0$ would show n-type conductivity. The prepared films are found to have Δy which are > 0 and therefore p-type conduction mechanism occurs in the $CuInS_2$ thin films [10, 24, 25]. This p-type nature may be attributed to Cu_{In} because the formation energy of V_{In} is larger compared to Cu_{In} [20]. On the other hand, the high mobility of Cu would promote the chemical diffusion of Cu leading to a change of composition of $CuInS_2$ and, in turn the type of conductivity, even at low temperatures, below 100 °C [26]. When Cu/In ratio and, consequently, the molecularity factor decreases, $CuInS_2$ films become more sensitive as reported by John *et al.* [1]. It is interesting to note that the comparatively lesser Cu/In ratio has been found for the films prepared at 60 °C than the films deposited at other temperatures.

3.3. Optical analysis of SILAR Cu-rich CIS thin films

Transmittance spectra and the plot of $(\alpha h\upsilon)$ versus $h\upsilon$ of CIS thin films deposited at different deposition temperatures are presented in Figs. 3 and 4, respectively. CIS films deposited at 60 °C (Fig. 3) are characterized by the lowest transmission coefficient and in turn higher optical absorption. The higher optical absorption is a key parameter regarding solar cell performance. It is well established that $CuInS_2$ is a direct band gap semiconductor with the band extrema located at the centre of Brillouin zone [27]. The estimated band gap energy values are presented in Table 4. The band gap energy of CIS thin films deposited at 60 °C has the value reported for single crystal (1.5 eV) whereas the band gap energies of the films deposited at other temperatures deviate slightly from the reported value of 1.5 eV, which may be due to poor crystallinity of the films. The evaluated value of refractive index (n) is in a good agreement with earlier reports [28] and shows a decreasing dependence on the wavelength (Fig. 5a), which is associated with an interband transition for photon energies smaller than the band gap [29]. It may be also due to the strong surface and volume imperfections on the microscopic scale [30].

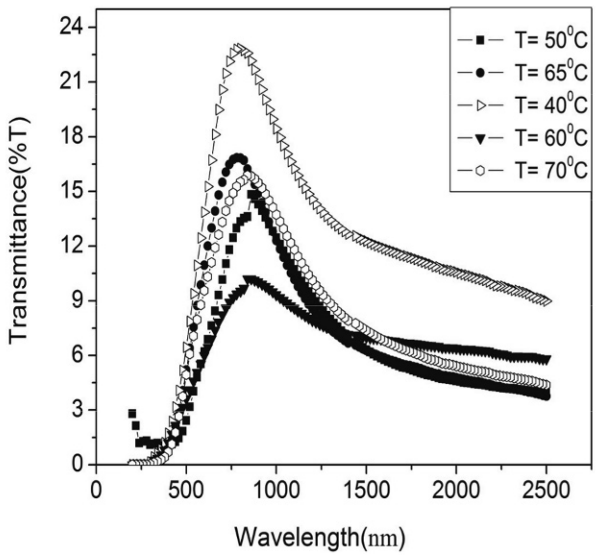


Fig. 3. Transmission spectra of SILAR Cu-rich CIS thin films.

Table 4. Optical parameters of CIS thin films.

Deposition temperature (°C)	E_g (eV)	E_0 (eV)	E_d (eV)	$n(0)$	k	ε_1	ε_2	ε_α	χ_e
				λ = 1000 Å					
40	1.52	3.04	31.65	3.76	0.24	14.14	1.81	149.18	10.74
50	1.52	3.04	31.40	3.87	1.13	13.69	8.79	83.31	5.54
60	1.50	3.00	19.00	2.93	0.87	7.87	5.11	70.28	4.96
65	1.53	3.06	18.86	2.87	1.76	5.15	10.18	108.87	8.25
70	1.47	2.94	6.67	2.89	0.77	7.77	4.46	87.65	6.35

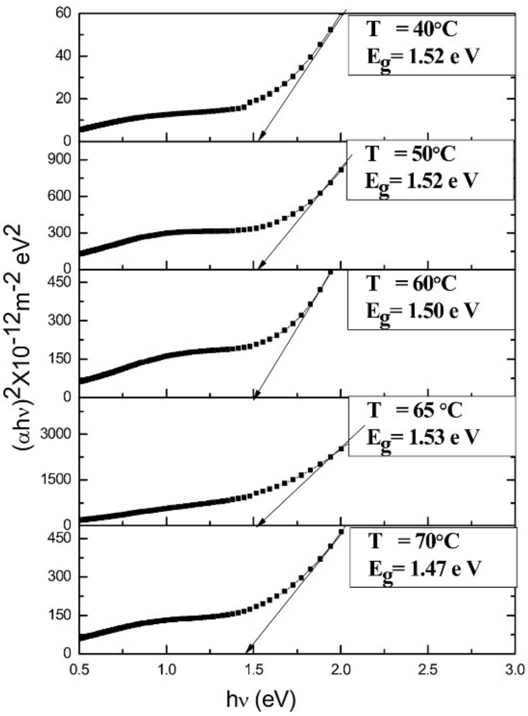


Fig. 4. Plot $(\alpha h\upsilon)^2$ *vs.* $(h\upsilon)$ of SILAR Cu-rich CIS thin films prepared at different deposition temperatures.

The refractive index of CIS thin films prepared at 60 °C (n = 2.93) is found close to the reported value (n = 3) [29].

The data on the dispersion of the refractive index were evaluated according to the single effective oscillator model proposed by Wemple and Di Domenico [31, 32]. It is well known from the dispersion theory that in the region of low absorption the index of refraction (n) is given in a single oscillator model by the expression [28],

$$n^2(h\upsilon) = 1 + \frac{E_d E_o}{E_o^2 - (h\upsilon)^2} \tag{5}$$

where $h\upsilon$ is the photon energy, E_o is the single oscillator energy and E_d is the dispersion energy which is a measure of the strength of interband optical transitions [33]. The oscillator energy E_o is an average energy gap and can be related to the optical band gap E_g with the equation $E_o = 2E_g$; the calculated energy values are given in Table 4.

The real and imaginary parts of the complex dielectric constants are evaluated using the relations [29],

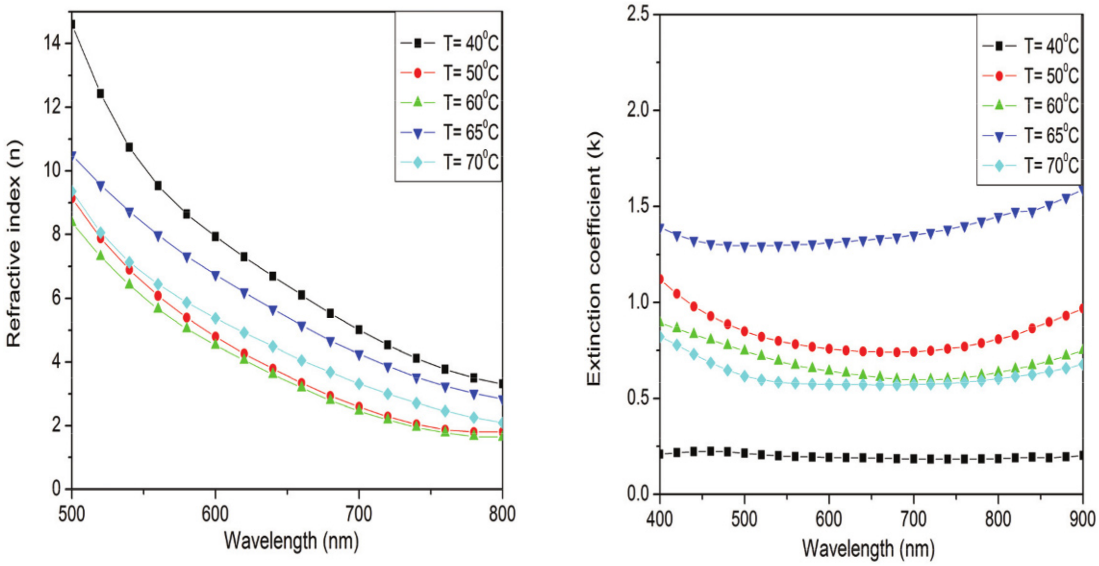
$$\varepsilon_1 = n^2 - k^2, \quad \varepsilon_2 = 2nk \tag{6}$$

and are presented in Table 4. For further analysis of the optical data, the contribution from the free carrier electric susceptibility χ_e to the real dielectric constant was analyzed according to Spitzer-Fan model and, on this basis, χ_e was determined (Table 4), using the relations [28],

$$\varepsilon_1 = n^2 - k^2 = \varepsilon_\alpha - \left[\frac{e^2}{\pi c^2}\right]\left(\frac{N}{m^*}\right)\lambda^2 \tag{7}$$

$$\left[\frac{e^2}{\pi c^2}\right]\left(\frac{N}{m^*}\right)\lambda^2 = -4\pi\chi_e \tag{8}$$

where ε_α is the high-frequency dielectric constant in the absence of any contribution from free carriers, χ_e is the electric free carrier susceptibility, N/m* is the carrier concentration to the effective mass ratio, e is the electronic charge and c is the velocity of light. The estimated ε_α, and χ_e values are presented in Table 4. The extinction coefficient (Fig. 5b) decreases and then slightly increases with wavelength (Table 4). The real and imaginary parts of dielectric constant decrease and become constant with wavelength (Fig. 6). Similar behaviour has been reported



(a) (b)

Fig. 5. Refractive index (n) and extinction coefficient spectra of Cu-rich CIS thin films.

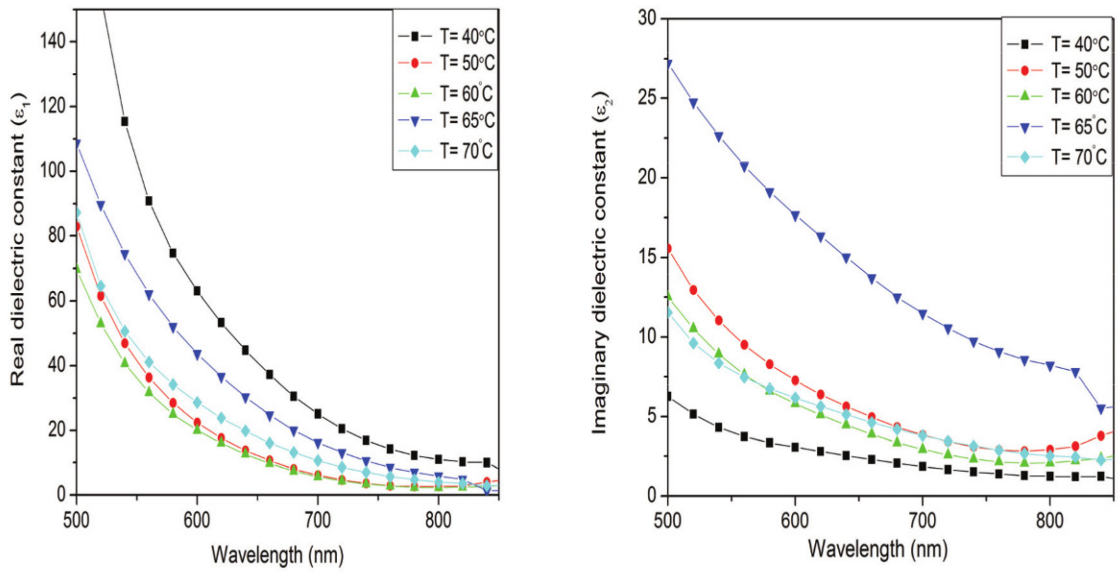


Fig. 6. Real and imaginary part of the dielectric constant spectra of Cu- rich CIS thin films.

earlier [28, 29] for CIS thin films prepared by thermal evaporation and spray pyrolysis. The higher values of extinction coefficient and imaginary dielectric constant may be due to higher absorption coefficient of Cu-rich CIS thin films. The existence of $k(\alpha\lambda/4\pi)$ and consequently ε_2 $(2nk)$ confirms that $CuInS_2$ films are not a loss free media [34] or good absorbers.

The values of dispersion energy of CIS films deposited at 60 °C and 65 °C are closer to the reported values [28]. Therefore, it is interesting to identify the deposition temperature range as 60 – 65 °C. It has also been found that the real parts of dielectric constant (ε_1) are higher that the imaginary parts (Table 4) as reported earlier [29]. The real part of dielectric constant for a film with E_g of 1.5 eV was reported earlier as 9.36. Since the estimated ε_1 value of the film deposited at 60 °C (7.87) is comparatively closer to the reported values, the deposition temperature has been chosen as 60 °C.

4. Conclusions

CIS thin films prepared at 60 °C have higher crystalline size and less defects such as dislocation density and strain. Lesser value of Cu/In and consequently molecularity factor observed in the film prepared at 60 °C reveal that the film prepared at that temperature is more stoichiometric and therefore more photosensitive compared to the films prepared at different temperatures. It is also interesting to note that optical parameters such as band gap energy, refractive index and real part of dielectric constants of CIS thin films deposited at 60 °C are closer to the reported values. Therefore, the optimum deposition temperature has been identified as 60 °C.

Acknowledgements

The authors wish to acknowledge the Secretary, Management and the Principal of Kongunadu Arts and Science College, Coimbatore for their constant support. One of the authors (M.D) wishes to thank UGC for the financial support extended sanctioning through a major research project in this explored area of Physics.

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Received 2012-07-10
Accepted 2013-01-25