STUDY OF SOME PHYSICAL PROPERTIES OF SPRAY PYROLYTICALLY DEPOSITED COPPER INDIUM DISULFIDE THIN FILMS

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ABSTRACT

Copper-indium-sulfide films were spray pyrolytically deposited from solutions containing cupric chloride, Indium tri-chloride and thiourea as an initial ingredient. The deposited films were characterized by x-ray diffraction, scanning electron microscopy and optical absorption techniques, respectively. The films structure was found to be tetragonal chalcopyrite with preferential orientation along (112) direction. Here by using x-ray diffraction data the micro structural parameters such as crystallite size, dislocation density and number of crystallite per unit cell were calculated. The variation of these parameters with and deposition composition were studied. Transmission spectra were carried out by UV-1800 Shimadzu spectrophotometer for the wavelength range 350 to 1100 nm. The band gap was found to be 1.43 eV which shows the direct allowed transition.

Keywords: Spray pyrolysis, Micro-structural parameters, Copper-Indium-sulfide thin films.

1. Introduction

I-III-VI$_2$ group material, ternary chalcopyrite compound is the leading semiconductor material due to low cost and abundance of the constituent element. This thin film of chalcopyrite find numerous applications in a variety of solid state devices such as visible and infrared light emitting diodes, solar cells, IR detectors and photovoltaic devices [Ishizaki, Saito, 2004; Marin, Wasim, Pèrez, Bocaranda, and Mora, 1998; Martinez, Fernández, Arriaga, Cano, 2006; Roy, Bhattacharjee, Kundu, Chaudhuri, Pal, 2003; Quiroga, Oentrich, Bonald, Medina, Wasin, Marin, 2003]. These group of compound are most promising candidates for application such as photo-voltaic power generation system because a) are direct band gap semiconductors with high absorption coefficient, b) can be easily obtained in the thin films form, Either n- type or p-type, c) have energy band gap (1-2 eV) in the optical range for solar energy conversion, d) have lattice constant which matches that of CdS, widely used in solar cell technology. The highest conversion efficiency of 19.9% was demonstrated for Cu(InGa)Se$_2$ based thin films solar cells with small area (<cm^2) [Marin, Wasim, 1998]. Roy et al [Roy, Bhattacharjee, 2003] pointed out that most of the ternary aqueous solutions can be used to prepared multilayer heterojunction thin films optoelectronic devices. The characterization of CIS thin films depends on native defects such as deviation of stoichiometry, deviation during fabricating films are required. This material is normally found to be p- type conducting. Cu-III-VI$_2$ thin films have been deposited using various technique; Chemical Bath Deposition method [Gupta, Pateria, Deshmukh, 2017], Hot Injection method [Vahishad, Ghasemzade, 2013], electrodeposition [Xu, Wang, 2011] and Spray Pyrolysis [Parameshwari, Bhat, 2012; Suriyanarayanan and Mahendran, 2012; Tembhurkar and Hirde, 1992].

We have chosen the economical and convenient method of chemical spray pyrolysis for the deposition of thin films. Typical spray pyrolysis equipment consist of an atomizer, precursor solution, substrate, heater and temperature controller. We have deposited CuInS$_2$ thin films by this method and study the optical band gap and structural properties with other microstructural parameters of the thin films. Thickness of the thin films was measured by Michelson Interferometer. We have used Shimazdu UV-1800 spectrophotometer to measure the optical transmission of the different substrate temperature (275^0C to 375^0C at the difference with 25^0C) was measured by pre-calibrated copper-constantan-thermocouple. XRD analysis was done using Bruker AXS D8 Advance X-Ray Diffractometer, with Cu Kα ($\lambda = 1.5418$ Å) radiation and maximum usable range 10 to 80 degree.

2. Materials and methods

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 and thiourea [$(NH_2)_2CS$] of purity 99 % MERCK Company on biological glass substrate kept temperature at 350^0C. The deposition was carried out onto commercially available glass substrate of the size $(7.5\times2.5\times0.1)$ cm^3. The analytical reagent grade chemicals were used. For preparing $CuInS_2$ thin film, we have mixed each solution in the ratio 1:1:3.2 by volume. Excess tellurium is necessary to obtain $CuInS_2$ the temperature of the substrate measured by a pre-calibrated copper constantan thermocouple was maintained and vary from 275^0c to 375^0c at the difference with 25^0C. The spray rate of 3.5 ml/min was maintained. The distance between the sprayer nozzle and substrate was 30 cm. The glass sprayer was mechanically moved to and fro during spraying to avoid the formation of droplets on the hot substrate and to ensure instant evaporation. The detailed experimental set up was explained [Tembhurkar and Hirde, 1992; Tembhurkar and Hirde, 1992]. The optical band gap was estimated by measuring optical transmission on Shimazdu UV-1800 spectrophotometer. The thickness of the films was measured by Michelson interferometer. XRD analysis was studied using Bruker AXS D8 Advance X-Ray Diffractometer.

3. Optical absorption

Plotting graph between $(\alpha h\nu)^2$ against hν for 350^0C temperature by using absorption spectral data obtained from UV-1800 Shimadzu Spectrophotometer of as deposited $CuInS_2$ thin film. The linear portion of each was extrapolated to meet energy (hν) axis given the value of band gap.

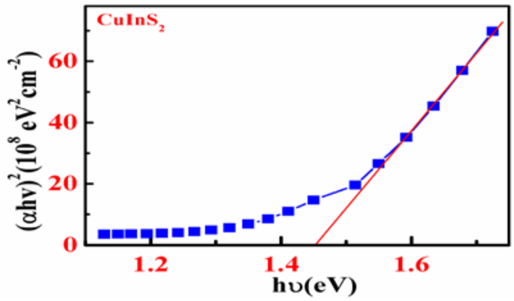

Fig 1. Variation of $(\alpha h\upsilon)^2$with incident photon energy (hv) for $CuInS_2$ thin films deposited at 350^0C

The band gap energy value (1.43 eV) for $CuInS_2$ films samples were determined from the optical spectra [Vahishad, Ghasemzadeh, 2013; Parameshwari, Bhat, 2012; Suriyanarayanan and Mahendran, 2012; Tembhurkar and Hirde, 1992]. Therefore, the observed Eg of 1.43 eV can be ascribed to $CuInS_2$, which is very close to the other reported values by other researchers [Parameshwari, Bhat, 2012; Tembhurkar and Hirde, 1992]. The minimum band gap energy of the crystalline material confirms the stability of the material. This result was in good agreement with results reported by Xu et al [Xu and Wang, 2011] and Parameshwari et al [Parameshwari, Bhat, 2012] for spray pyrolytically deposited $CuInS_2$ thin films.

4 .Optical Constants

The optical behavior of materials utilized to determine its optical constants (refractive index (n), extinction coefficient (k), real and imaginary parts of dielectric constants (ε_1, ε_2) and have wide applications in designing different optical components and modeling optical. In the present study, determine the optical constants; for that purpose there was used UV-1800 Spectrophotometer for the measurements of reflectance (R) and transmittance (T) of sample in the wavelength range 350 nm to 1100 nm and the extinction coefficient can be calculated. Therefore we are used following equation to calculate optical constant for different temperature (250 to 375 at the interval of 25^0C prepared sample of $CuInS_2$,

For non-magnetic materials, we can take $\mu = 1$, the real and imaginary part of dielectric constant can be calculated by using the following equations,

$\boldsymbol{\varepsilon} = \varepsilon_1 + i\varepsilon_2 = (n + ik)^2$ (1)

$(n - ik)^2 = \varepsilon - i\varepsilon$(2)

Where, $\varepsilon_1 = n^2 - k^2$ (3)

and $\varepsilon_2 = 2nk$ (4)

Where, n is the refractive index and k is the extinction coefficient and where we note that they are all frequency dependent.

The refractive index value can be calculated from the formula [AL- Jubory, 2012],

$n = (1+R/1-R) + [4R/(1-R)^2 - k^2]^{1/2}$ (5)

Next, in order to complete the calculation of the optical constants, the extinction coefficient (k)is estimated from the values of absorption coefficient (k) and wavelength (λ),

$k = \frac{\alpha\lambda}{4\pi}$ (6)

Where λ is the wavelength of the incident radiation and absorption coefficient (α)

Using these equations (1-6), calculate all these values of optical constants and reported in table 1.

Table. 1 Tabulated values of Extinction Coefficient (k) and Refractive Index (n) real and imaginary part of Dielectric constant and other parameters with various temperatures.

Films	T (^{0}C)	Thickness	Eg (eV)	Extinction Coefficient (k)	Refractive Index	Dielectric constant ε1	ε2
$CuInS_2$	250	0.1432	1.56	0.40-1.92	1.41-1.22	10.11-0.99	1.15-3.52
	275	0.1686	1.52	0.40 -1.92	1.32-1.22	9.95-0.25	7.84-3.46
	300	0.1733	1.47	0.351-2.381	1.38-1.22	10.11-0.22	5.45-2.25
	325	0.1752	1.45	0.31-2.21	1.39-1.22	10.14-0.77	5.07-2.01
	350	0.1862	1.43	0.65-2.29	1.28-1.22	9.81-0.50	5.24-4.18
	375	0.1756	1.63	0.005-0.039	1.51-1.24	10.24-1.30	0.03-0.09

5. X-ray study

Fig. 1 shows the X-ray diffraction pattern of as deposited of $CuInS_2$ thin films. In the present study, XRD analysis was done using Bruker AXS D8 Advance X-Ray Diffractometer, with Cu Kα (λ = 1.5418 Å) radiation and maximum usable range 10 to 80 degree. The X-ray diffraction technique is used to discuss the structural properties of these films. The observed diffraction peaks of $CuInS_2$ thin film were found at 2θ values of angles 27.90^0, 29.12^0, 32.18^0, 37.13^0, 46.32^0, 50.01^0, 60.65^0 corresponding to the lattice planes [112], [200/400], [211], [301], [116/312], [231/107], [235/413] and [420/404] respectively. This agrees well with the JCPDS File no-65-2732. Each diffraction peak of annealed films shows sharp. XRD studies revealed that the films of $CuInS_2$ are polycrystalline in nature with Tetragonal chalcopyrite structure with lattice constant a = 5.5507 Å and c = 11.090 Å. The different peaks in the diffractogram were indexed by usual method. The corresponding values of inter-planar spacing‘d’ were calculated and compared with standard JCPDS data [Card No. 65-2732]. The crystalline size was estimated from the Scherrer equation [Parameshwari, Bhat, 2012], the crystallite size increased 0.1 to 0.2 μm.

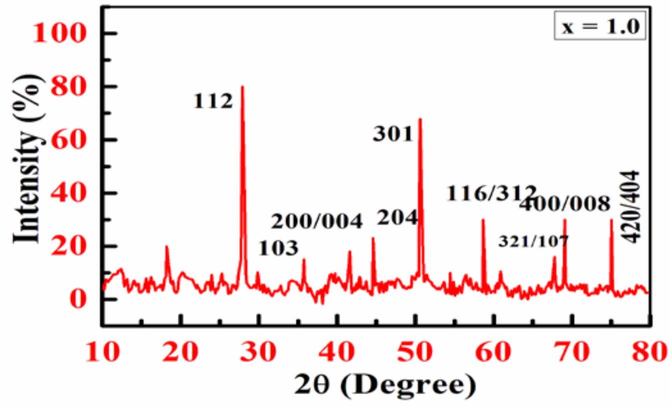

Fig 2.XRD pattern of all composite thin films of $CuInS_2$

These values of‘d’ compared with JCPDS data [Card No. 65-2732] were examined for identification of $CuInS_2$ thin films. The lattice parameter a = 0.55507 nm and c = 1.1090 nm values calculated and distortion (Δ) = 2-c/a = 0.00205. The values of ‘a’ and ‘c’ were in good agreement with the JCPDS data for $CuInS_2$ [Chaki and Agarwal, 2007] thin films.

Many researchers [Vahishad, Ghasemzadeh, 2013; Parameshwari, Bhat, 2012] worked on $CuInS_2$ by spray pyrolysis method and other techniques [Marin, Wasim, 1998; Rabeh, Kanzari, 2009; Chaki and Agarwal, 2007; Landry and Lockwood, 1995; Soliman, 1994], they also found that the well agreed results. Tembhurkar et al [Tembhurkar and Hirde, 1992] reported values value was in small and negative to indicate built-in dilation condition. In each case, the intensities of $CuInS_2$ thin films depend upon the concentrations of chemical compounds [Landry and Lockwood, 1995; Kazmerski and Ayyagari, 1976; Lontchi, Khalfallah, 2016].

The dislocation density (δ) is defined as the length of dislocation lines per unit volume of the crystal and was calculated using Williamson-Smallman relation [Purohit, Chander, 2015; Mahalingam, Thanikaikarasan, 2010],

$$\delta = \frac{1}{D^2} \qquad (7)$$

where, D is the particle size

The internal strain (ε) was calculated using the relation concerned [10, 24],

$$\varepsilon = \beta \cos\theta/4 \qquad (8)$$

Number of Crystallites per unit area (N),

$$N = t/D^3 \quad (9)$$

Where, t- thickness of as-deposited thin films, D-grain size, crystallite Size

Table. 2 Variation of crystallite size (D), Dislocation density (δ), Internal strain (ε) and (N) with temperature for $CuInS_2$ thin films.

Films	T (^{0}C)	Thickness (µm)	Crystallite size (D) (10^{-10}) (m)	Dislocation Density (δ) (10^{10}) (m^{-2})	Internal Strain (ε) (10^{-6}) (m^{-2})	N (10^8) (m^{-3})
$CuInS_2$	250	0.1432	7.2351	1.9103	5.0078	3.7810
	275	0.1686	7.7169	1.6792	4.6951	3.6688
	300	0.1733	7.8016	1.6429	4.6441	3.6496
	325	0.1752	7.8808	1.6101	4.5975	3.5795
	350	0.1862	8.1272	1.5394	4.45811	3.4686
	375	0.1756	8.5315	1.3738	4.2468	2.8277

It was observed that films to be well crystalline with preferential orientation along (112) direction. In As deposited and annealed thin films of $CuInS_2$, the intensity of the peaks increased and width of the peak decreased. Our calculated values of lattice parameter well agree with results reported by other workers [Quiroga, Oentrich, 2003, AL- Jubory, 2012 and Chaki and Agarwal, 2007].

The variation of dislocation density and number of crystallites per unit area (N) with temperature and parameter x for thin films of the $CuInS_2$are found to decrease while increasing temperature from 275ºC to 350ºC. This information of crystallite size and other parameter of the films were obtained from the full-width at half maxima of the diffraction peaks. It is also observed (from table 2) the crystallite size increases with increasing temperature for preparation of films [Chen, Lu, 2005; Reshak and Auluck, 2008]. Due to the defects in the lattice with increase in temperature the strain in the film gets released and attained a maximum value at 375ºC.

The strain developed at higher substrate temperatures is likely to be due to the formation of native defects developed from the lattice misfit or dislocations. A sharp increase in crystallite size and decrease in strain with variation of temperature indicated in table (2). Such a release in strain reduced the variation of interplanar spacing thus leads to decrease in dislocation density of all these thin films and minimum values are obtained for films deposited at 375ºC.

From the above observation, the dislocation density decreases with increase crystallite size. Due to the annealing, the films became more stoichiometric. Murali et al [Murali, Muthusamy, 2013] were well agreed to this reported result in present work and earlier by other workers [Reshak and Auluck, 2008]. There was calculated dislocation density, internal strain, crystallites size and other parameters were studied.

6.Conclusion

In conclusion, it is established that $CuInS_2$ thin film of good quality with stoichiometry close to 1:1:2 can be prepared by spray pyrolysis method the film deposited at optimized substrate temperature 250 to 350^0C at interval of 25^0C and concentration of 0.02 M are polycrystalline having energy band gap 1.43 eV. In structural studies shows that the deposited films possess tetragonal chalcopyrite structure with preferential orientation along 112 direction. The microstructural parameters such as crystallite size, dislocation density and number of crystallite per unit cell were evaluated and are found to be depending upon the deposition conditions. The observed variation in optical constants for $CuInS_2$ films with deposition temperature is due to corresponding variation in particle size and film thickness with deposition temperature. The band gap values, optical constant, structural properties with microstructural parameters of $CuInS_2$ thin films obtained in this paper and all these values is good agreed with the other reported earlier.

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