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Preparation, structural parameter and band gap variation of spray pyrolytically deposited $CuInTe_{2(1-x)}S_{2x}$ thin films

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ABSTRACT

Spray pyrolysis is simple and inexpensive method to prepared thin films on large area. $CuInTe_{2(1-x)}S_{2x}$ thin films were deposited by this method. Optical band gap was determined for composition parameter x from the transmittance study at room temperature. Optical band gap increases as composition x increases and it is vary linearly with composition. The lattice parameter a and c were calculated for all composition x from the Philips X-ray diffractometer. The structure remains tetragonal chalcopyrite throughout the composition x with preferred orientation along 112 direction. Tetragonal distortion is very small and negative indicating dilation (c>2a) rather than compression

Keywords: Ternary semiconducting thin films, Spray pyrolysis, Chalcopyrite structure, Optical properties

INTRODUCTION

Ternary semiconducting compounds of I-III-VI_2 class were crystalline in the tetragonal chalcopyrite structure. This group of compounds shows interesting properties in photovoltaic conversion [1] and their alloy because of their possible technological application for example in solar energy conversion. The other researchers [2-5] have studied in some detail the crystallographic properties and optical energy band gap values of solid solution, $Cu(In,Ga)Se_2$,Cu-In-Ga-Se(Te), $CuIn(S_xSe_{1-x})_2$.

Shay and Wernick [6] noted in I-III-VI_2 group of compound and observed that there has structure which is super-lattice of cubic Zinc-blende structure enables them to be used in non-linear optical application, photovoltaic extension of tetragonal diamond-like zinc-blende form, which make them useful for lattice matching to other semiconductors. Therefore, they are of a great technological interest in the field of photovoltaics, optical detectors and lasers. Romeo et al [7] stated that in $CuGaSe_{2(1-x)}Te_{2x}$ for x = 0.675 has a minimum lattice mismatch with CdS and at the same time has a band gap of 1.45 eV [8] in the optimum energy range for solar energy conversion. Keeping this in mind, in the present case $CuInS_2$ and $CuInTe_2$ the energy band gap 1.43 eV [9] and 0.99 eV [10] respectively and their solid solutions were selected and studied. In all the above investigations the sample materials was prepared from elements by usual melt and anneal technique. Moreover, all the previous studies [11-13,] studied the tetragonal distortion of the solid-solution of telluride, selenide and sulphide in the form of thin films grown by flash evaporation and spray pyrolysis respectively.

In this paper we report the preparation, characterization, lattice constant and optical band gap determination of solid solutions of the type $CuInTe_{2(1-x)}S_{2x}$ for $0 \leq x \leq 1$ where x is the composition variable which gives the fractional concentration in the form of thin films by spray pyrolysis. Spray pyrolysis is a simple, inexpensive, convenient method to deposit thin films on large area. The temperature was measured by pre-calibrated copper-constantan thermocouple. Thickness of the films was measured by Michelson interferometer. The absorption edge analysis was carried out by using transmittance vs wavelength on UV-1800 Shimadzu Spectrophotometer. Lattice parameters a and c were determined on Philips X-ray diffractometer using CuK_α radiation with wavelength 1.542 Å.

MATERIAL AND METHODS

Aqueous solutions of cupric chloride, Indium tri-chloride, Thiourea and Tellurium tetra-chloride were used for

spraying the film on hot glass substrates. The chemical were used of AR-Grade. The molarity of each solution was 0.02 M. They were mixed together in the ratio 1:1:3.2 by volume. The excess sulphur and tellurium was necessary to obtain $CuInTe_{2(1-x)}S_{2x}$ films. The deposited films showed sulphur and Tellurium deficiency, when the ratio of solution was taken as 1:1:2. The excess elements were used to remove this deficiency [5, 9 and 13]. The composition parameter x was varied from 0 to 1 in steps of 0.25. Biological glass slide (1.30 mm thick) were used as the substrate. The temperature of the substrate was maintained at 350^0c and measured by pre-calibrate thermocouple. The distance between the sprayer nozzle and substrate was maintained was 30 cm. Spray rate was maintained at 3.5 ml/min and the spraying was done in air at 12 kg/cm^2 pressure. The glass sprayer moved to and fro during to avoid the formation of droplets on hot substrate and to ensure instant evaporation [14].

RESULTS AND DISCUSSION

Optical studies

The transmittance (T %) of the films was measured at room temperature on UV-1800 Shimadzu spectrophotometer. A glass plate identical to the substrate was placed in the path of the reference beam and a substrate with deposited thin films was placed in the path of the sample beam. The variation in transmission with wavelength of incident beam was recorded for the wavelength range 350 nm to 1100 nm. Figure 1 shows the transmission (T %) vs wavelength (λ) variation for different composition x. The transmittance was constant for higher wavelength and started decreasing after the particular wavelength, depending upon the composition parameter x. The onset of decrease of transmittance gives the fundamental absorption edge [13]. This onset of decrease of transmittance is indicated by an arrow on each transmittance curve in Figure 1. It was observed that this arrow shifted towards the lower wavelength side as composition parameter x increased. The absorption coefficient (α) at various wavelengths for a sample of thickness (t) is given by the relation,

$$\alpha t = \ln(I_0/I) \quad (1)$$

where I_0 and I be the intensities of incident and transmitted radiation respectively. It is seen from figure that interference effects can be neglected for films deposited on thick non-absorbing substrate. The value of α at various wavelengths for all values of x was calculated from the transmission curve using relation (1).

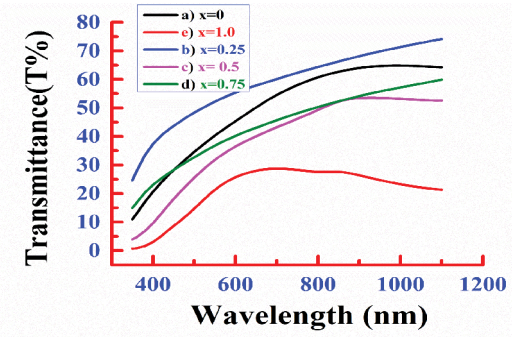

Figure 1: Transmittance v/s Wavelength with different proportion a) x = 0, b) x = 0.25, c) x= 0.5, d) x= 0.75, e) x= 1.0

The $(\alpha h\nu)^2$ was plotted against hν near and above the fundamental absorption edge as shown in Figure 2. Each graph had some linear portion above the fundamental edge, which extrapolated on hν axis gave the value of band gap. The linear relation indicates that a direct allowed transition, described by the relation,

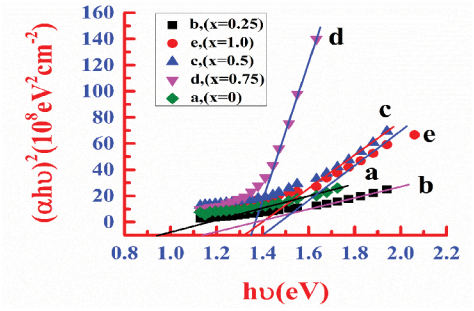

Figure 2: Plot of $(\alpha h\nu)^2$ against hν for A) x=0, B) x = 0.25, C) x = 0.50 D) x = 0.75 and E) x = 1.0

$$\alpha = \frac{A_1}{h\nu}(h\nu - E_g)^{1/2} \quad (2)$$

was probably responsible for the absorption process. Figure 3 shows that the band gap values obtained were 0.98 eV, 1.16 eV, 1.26 eV, 1.32 eV and 1.42 eV for x = 0, 0.25, 0.50, 0.75 and 1.0 respectively. The band gap for x = 0 i.e. $CuInTe_2$ was fairly in good agreement with the result obtained by Boustani et al [14], who have reported the value of band gap as 0.97 eV for thermal vacuum evaporation from a single source and for flash evaporation respectively while other workers [15, 16] also reported the value of the band gap lies between 0.93 eV to 1.03 eV for different preparation technique. This lower value of optical band gap may be due to the existence of tail states and traps. Similarly the optical band gap for x =1 i.e. $CuInS_2$ was close agreement with other workers [17,18] who demonstrated that the optical band gap was 1.44 eV and 1.38- 1.43 eV respectively for spray pyrolytically deposited films.

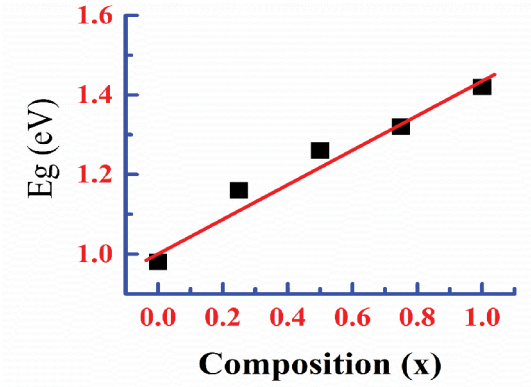

Figure 3: Plot Energy band gap (Eg) against Composition (x)

It was also observed that the band gap varied linearly with composition parameter x Figure 3. This results well agree with result reported by Tembhurkar et al [5] for $CuInSe_{2(1-x)}S_{2x}$ by spray pyrolysis method. One of the researcher Shewchun et al [19] studied $A^{I}_{1-y}B_yC^{III}D^{VI}_{2x}E_{2(1-x)}{}^{VI}$ quaternary alloy system and have drown contour map for iso-band gap and iso-lattice constant at 300 and 77 K. They used solution of any two of the $AgInSe_2$, $AgInS_2$, $CuInSe_2$ and $CuInS_2$ compounds. From these iso-band gap plots, if we find the variation of parameter x with band gap, keeping y constant, we get a straight line. However the variation of band gap with composition parameter y for x = constant was parabolic. Our result indicating the linear variation of band gap with x tallied with the observation of [19] for y = 0.

Structural properties

X-ray diffraction studies confirmed that all the five composition film had a tetragonal chalcopyrite structure with the preferred orientation along the 112 direction. The typical X-ray diffraction obtained for $CuInTe_{1.5}S_{0.5}$ $CuInTe_{0.5}S_{1.5}$ is shown in Figure 4 and Figure 5.

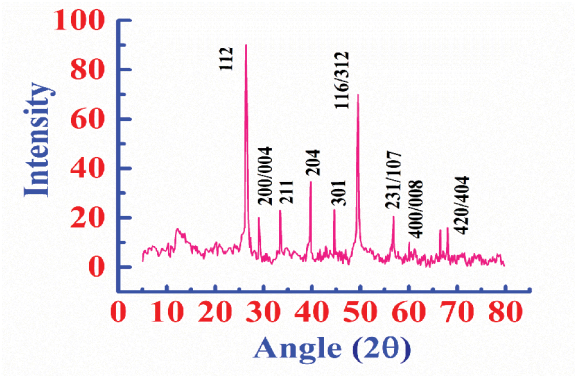

Figure 4: X-ray diffraction pattern of as deposited $CuInTe_{2(1-X)}S_{2X}$ thin films for x = 0.25

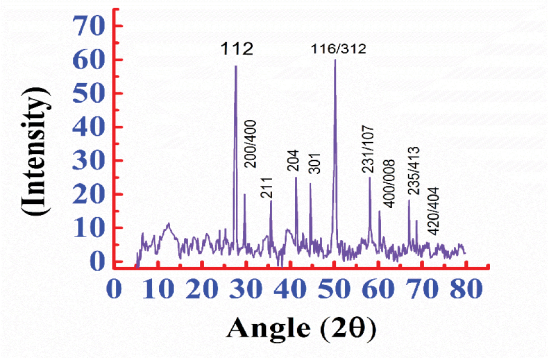

Figure 5: X-ray diffraction pattern of as deposited $CuInTe_{2(1-X)}S_{2X}$ thin films for x= 0.75,

Each line on diffraction pattern is indexed by usual procedure and lattice constant were determined by the least squares fitting procedure. Lattice parameter a and c and tetragonal distortion (Δ) were calculated from X-ray diffraction peaks (Table1).

The experimental values of both a and c (table1) could be best fitted by a quadratic equation of the form,

$$P = \alpha+\beta x+\gamma x^2,\ 0\leq x\leq 1 \qquad (3)$$

Where, P is the parameter a or c and not by a linear equation as expected from Vegard's law. The variation of lattice parameter a and c with composition parameter x as shown in Figure 6 and Figure 7. The points are the experimental points and the solid lines are the lines fitted to the equation (3).

Table 1: Lattice Constant a and c for the system $CuInTe_{2(1-x)}S_{2x}$

X	Compounds	Eg (eV)	a (nm)	c (nm)	c/a	Δ = 2-c/a
0	CuInTe2	0.98	0.61798	1.23596	1.99902	0.00098
0.25	CuInTe1.5S0.5	1.16	0.6144	1.2288	2	0
0.50	CuInTe1.0S1.0	1.26	0.6124	1.2218	1.99510	0.0049
0.75	CuInTe0.5S1.5	1.32	0.6065	1.2130	1.99835	0.00165
1.0	CuInS2	1.42	0.6038	1.2076	2	0

Table 2: Fitted Coefficient of Equation (2) for the system $CuInTe_{2(1-x)}S_{2x}$

Lattice Parameter	α (nm)	B (nm)	γ (nm)	σ $(Ohm\text{-}cm)^{-1}$
a	0.61798	0.0118	0.002294	2.9064×10^{-4}
b	1.23596	0.0253	0.00301	0.11948×10^{-4}

Table 2 gives the relevant fitting parameter together with the expected error. This linear variation of lattice parameter with composition x follows Vegard's law. This result was in good agreement with that of Shay and Wernick [6] for a single crystal. Our values of a and c for $CuInTe_2$ (x = 0) and $CuInS_2$ (x =1) are well agreed with JCPDS data (file card no. 34-1498 and 65-2732). Similar result reported by Tembhurkar et al. [5] for solid solution $CuInSe_{2(1-x)}S_{2x}$ by spray pyrolysis method. Avon et al. [22] have studied thoroughly the multinary system $Cu_{1-x}Ag_xIn_{1-y}Se_{2(1-z)}Te_{2z}$. They have reported the lattice constant values for about 125 alloys within this group. They found a quadratic variation of lattice constant with the composition parameter they also found that miscibility gaps existed on the gallium face of the alloys. Our calculated value of tetragonal distortion (Δ) less than or equal to 0.001. This result agreed well with Robbins et al [23] who have studied the systems $CuM^{III}X_2^{VI}$ where M^{III} = In, Al and Ga, X^{VI} = Te, Se and S and they suggested that when the difference in the lattice constant ratio, Δ = 2-c/a, for two ternaries is less than or equal to 0.13, would these compounds show complete solid solubility in all compositions. The miscibility gaps in the work of Avon et al [22] are consistent with these conditions. In our result tetragonal distortion was small and negative, which indicated built in dilation (c>2a) rather than compression [5] as the usual case.

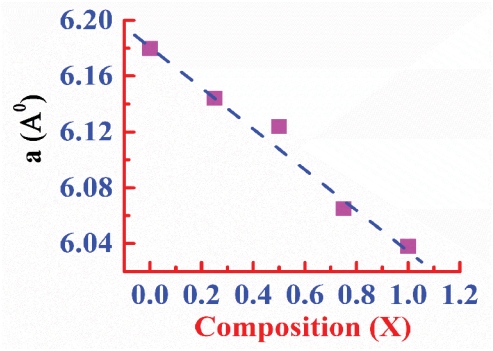

Figure 6: Variation of lattice constant "a" against composition variable (x)

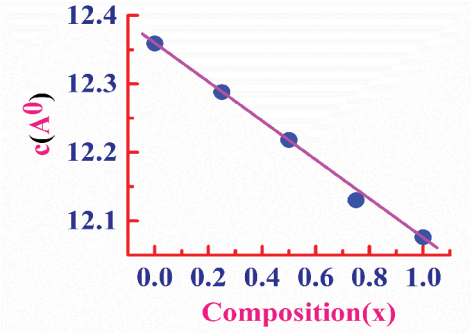

Figure 7: Variation of lattice constant "c" against composition variable (x)

CONCLUSIONS

We conclude that spray pyrolysis is simple and successful method for growing thin films of $CuInTe_{2(1-x)}S_{2x}$. The structure of the films is predominantly chalcopyrite with preferred orientation along the 112 direction. Structural parameter a and c and optical band gap vary linearly and not parabolic with composition parameter x. Tetragonal distortion is small and negative for all values of x indicating built in dilation (c > 2a) rather than compression.

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