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Band gap and structural parameter variation of $CuInSe_{2(1-X)}S_{2X}$ solid-solution in the form of thin films

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Abstract. $CuInSe_{2(1-X)}S_{2X}$ thin films were deposited by spray pyrolysis. Lattice parameters a and c, for all composition parameters X, were calculated from the Phillips X-ray diffractometer. The structure remained tetragonal chalcopyrite throughout. Optical band gap (E_g) was determined for the composition parameter X from the transmittance study at room temperature. Variation of E_g, a and c with X was found to be linear.

Keywords. Ternary semiconductor compounds; spray pyrolysis; chalcopyrite structure.

1. Introduction

Ternary semiconductor compounds of I–III–VI_2 class were crystallized in chalcopyrite structure. These compounds were of great importance due to their applications in opto-electronic devices. The properties of these compounds have been investigated for crystalline form and also for thin film form. Many workers (Shewchun *et al* 1979; Avon and Wooley 1981; Avon *et al* 1984; Annapurna and Reddy 1986) have studied solid-solutions of ternary sulphides, selenides and tellurides of the type, $A^{I}_{1-X}B^{I}_{X}C^{III}_{1-Y}D^{III}_{Y}E^{VI}_{2Z}F^{VI}_{2(1-Z)}$ for various values of compositional parameters X, Y, Z. The tetragonal distortion and optical band gap variation for different values of compositional parameters X, Y, Z have been reported and an attempt made to relate the values of tetragonal distortion with electronegativity of the atoms involved. Phillips (1974) proposed that the relation,

$$\Delta = -0{\cdot}60\,X_{I} + 0{\cdot}25\,X_{III} + 0{\cdot}15\,X_{VI} + 0{\cdot}01 \tag{1}$$

should apply, where X_I, X_{III} and X_{VI} were the electronegativity values (Phillips 1973) of the I, III and VI atoms respectively and $\Delta(=2-c/a)$, the tetragonal distortion. Weaire and Noolandi (1975) have suggested the relation,

$$\Delta\alpha(X_{I} - X_{III})^2. \tag{2}$$

The validity of (1) and (2) for different solid-solutions of the above type was tested by Avon *et al* (1984). In all the above investigations the sample material was prepared from elements by the usual melt and anneal technique. The samples were annealed for 2–3 months before the final measurements. Sridevi (1984) studied the tetragonal distortion of the solid-solution of tellurides and selenides in the form of thin films grown by flash evaporation method.

Spray pyrolysis was a comparatively cheap and convenient method for deposition of thin films. This paper reports our studies on the band gap and tetragonal distortion of solid-solutions of two ternary chalcopyrites $CuInSe_2$ and $CuInS_2$ in the form of spray pyrolytically deposited thin films. The thickness of the film was measured by Michelson interferometer. The absorption analysis was carried out using transmittance

vs wavelength data on a Hitachi spectrophotometer (model 330 UV–VIS–NIR). Lattice parameters a and c were determined on a Phillips X-ray diffractometer using CuK_α radiation.

2. Preparation of samples

Aqueous solutions of cupric chloride ($CuCl_2 2H_2O$), indium trichloride ($InCl_3$), thio-urea (H_2NCSNH_2) and seleno-urea ($H_2NCSeNH_2$) were used for spraying the films on hot glass substrates. The molarity of each solution was 0·003 M. They were mixed together in the ratio of 1:1:3·2 by volume. Excess sulphur and selenium was necessary to obtain $CuInSe_{2(1-X)}S_{2X}$ films. The deposited films showed sulphur and selenium deficiency, when the ratio of solutions was taken as 1:1:2. Excess sulphur and selenium (in the form of thio-urea and seleno-urea) were used to remove this deficiency (Rajaram *et al* 1983). The composition parameter X in $CuInSe_{2(1-X)}S_{2X}$ was varied from 0 to 1·0 in steps of 0·25. Biological glass slides (1·30 mm thick) were used as the substrate. The substrate temperature was maintained at 350°C and measured by pre-calibrated thermocouple. The distance between the sprayer nozzle and substrate was 30 cm. Spray rate was maintained at 3·5 ml/min and the spraying done in air at 12 kg/cm^2 pressure. The glass sprayer was mechanically moved to and fro during spraying to avoid the formation of droplets on hot substrate and to ensure instant evaporation.

3. Absorption edge analysis

The optical transmission (T) was recorded at room temperature using the same spectrophotometer. The transmittance curves for the wavelength range of 350 to 1600 nm are shown in figure 1. The transmittance was constant for higher wavelengths and started decreasing after a particular wavelength, depending upon the composition parameter X. The onset of decrease of transmittance represents the fundamental absorption edge (Hirde and Tembhurkar 1990). This onset 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 X increased.

The absorption coefficient (α) at various wavelengths for the sample thickness (t) is given by the relation,

$$\alpha t = \ln(I_0/I) \tag{3}$$

where I_0 and I are the intensities of incident and transmitted radiation respectively. The value of α at various wavelengths for all values of X was calculated from the transmission curve using relation (3) above. To calculate the exact value of band gap, a graph $(\alpha h\nu)^2$ against $h\nu$ was plotted for the region near and above the fundamental absorption edge (figure 2). Each graph had some linear portion above the fundamental absorption edge, the extrapolated intercept on $h\nu$ axis gave the value of band gap. The linearity of the graph indicated that the directly allowed transition described by the relation,

$$\alpha = A/h\nu(h\nu - Eg)^{1/2} \tag{4}$$

was probably responsible for the absorption process. The band gap values obtained

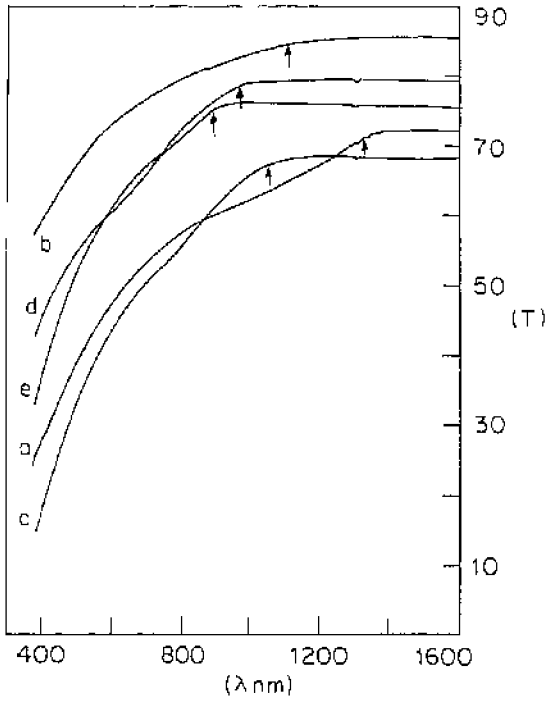

Figure 1. Transmission T as a function of the wavelength for: (a) $X = 0$, (b) $X = 0{\cdot}25$, (c) $X = 0{\cdot}50$, (d) $X = 0{\cdot}75$ and (e) $X = 1{\cdot}0$.

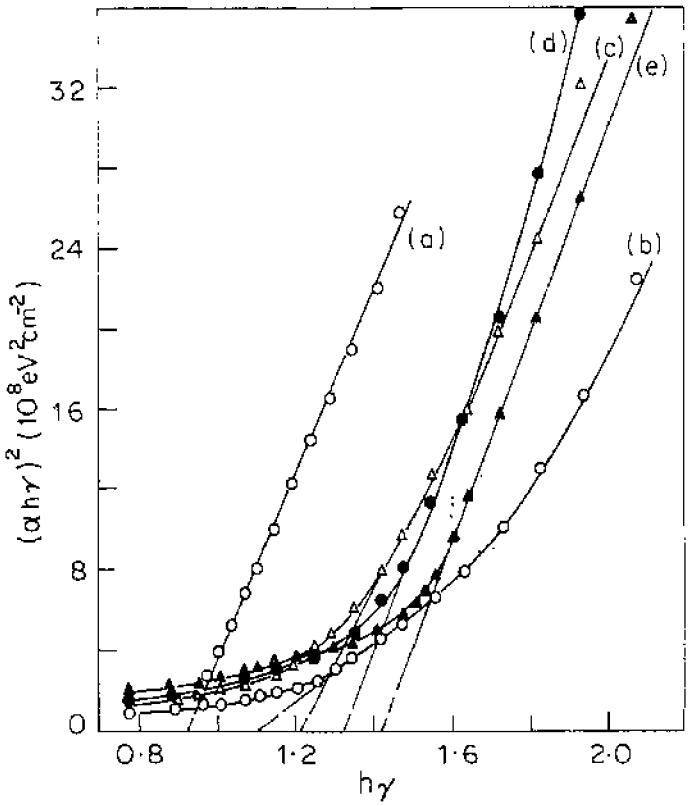

Figure 2. Plot of $(\alpha h\nu)^2$ against incident photon energy ($h\nu$) for: (a) $X = 0$, (b) $X = 0{\cdot}25$, (c) $X = 0{\cdot}50$, (d) $X = 0{\cdot}75$ and (e) $X = 1{\cdot}0$.

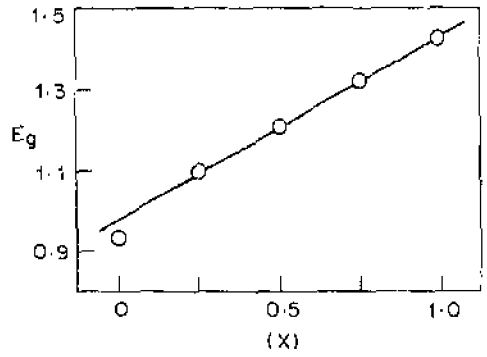

Figure 3. Plot of band gap against composition parameter X.

were 0·93, 1·1, 1·22, 1·33 and 1·43 eV for $X = 0$, 0·25, 0·50, 0·75 and 1·0 respectively. The band gap for $X = 0$ i.e. $CuInSe_2$ was in fairly good agreement with that of Joiet *et al* (1985) and Padam (1987) who reported a value of 0·90 eV. Similarly the band gap for $X = 1$ i.e. $CuInS_2$ was in close agreement with that of Rajaram *et al* (1983) and Hiroyoshi and Miyashita (1984), who demonstrated that the band gap was 1·44 and 1·38–1·43 eV respectively for spray-pyrolytically deposited films.

It was observed that the band gap varied linearly with composition X (figure 3). Shewchun *et al* (1979) studied the $A^{I}_{1-Y}B_Y C^{III} D^{VI}_{2X} E^{VI}_{2(1-X)}$ quinary alloy system and have drawn contour maps for iso-band gap and iso-lattice constant at 300 and 77 K. They used solid-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 results indicating the linear variation of band gap with X tallied with the observations of Shewchun *et al* (1979) (for $Y = 0$).

4. Lattice constant a and c by X-ray diffraction

X-ray measurements were carried out on a Phillips X-ray diffractometer using CuK_α radiation with wavelength 1·542 Å. X-ray diffraction studies confirmed that all the five composition films had a tetragonal chalcopyrite structure, with preferred orientation along the 112 direction. Lattice parameters (a and c) and tetragonal distortion (Δ) were calculated from X-ray diffraction peaks (table 1). Figure 4 shows the plot of variation of lattice parameters a and c with X. It was observed that lattice parameters a and c varied linearly with composition. This linear variation of lattice parameters with composition X follows Vegard's law. This result was in good agreement with that of Shay and Wernick (1975) for a single crystal. Our values of a and c for $CuInS_2 (X = 1)$ and $CuInSe_2 (X = 0)$ agreed well with ASTM data.

As a and c vary linearly, we can write expressions for the parameters a and c at composition parameter X as follows

$$a = a_0 + (a_1 - a_0)X = a_0(1 + \varepsilon X), \tag{5}$$

$$c = c_0 + (c_1 - c_0)X = c_0(1 + \delta X), \tag{6}$$

Table 1. Lattice parameters and tetragonal distortions of $CuInSe_{2(1-X)}S_{2X}$ thin films.

Composition variable X	Thin films	a (nm)	c (nm)	c/a	Δ
0·00	$CuInSe_2$	0·5771	1·1563	2·0036	−0·00363
0·25	$CuInSe_{1·5}S_{0·5}$	0·5716	1·1448	2·0027	−0·00279
0·50	$CuInSe_{1·0}S_{1·0}$	0·5625	1·1353	2·0183	−0·01831
0·75	$CuInSe_{0·5}S_{1·5}$	0·5589	1·1202	2·0042	−0·00429
1·00	$CuInS_2$	0·5524	1·1105	2·0103	−0·01031

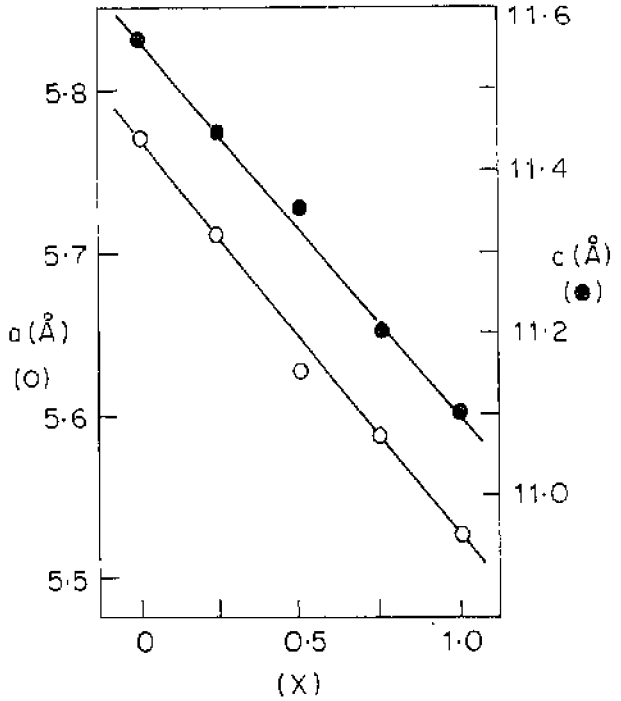

Figure 4. Variation of lattice constant a and c against composition variable X.

where a_0, c_0 and a_1, c_1 are the parameters at compositions $X = 0$ and 1.

$$c/a = (c_0/a_0)(1 + \delta X)(1 - \varepsilon X + \varepsilon^2 X^2 + \ldots)$$
$$= (c_0/a_0)[1 + (\delta - \varepsilon)X + \varepsilon^2 X^2 - \delta\varepsilon X^2] \quad (7)$$

neglecting higher orders of ε and δ. Substituting the values of $\delta = -0{\cdot}0396$ and $\varepsilon = -0{\cdot}0428$ in (7) we get

$$c/a = (c_0/a_0)(1 - 0{\cdot}0032\,X + 0{\cdot}00183\,X^2 - 0{\cdot}00169\,X^2)$$
$$= (c_0/a_0)(1 - 0{\cdot}0032\,X - 0{\cdot}00014\,X^2). \quad (8)$$

The parabolic term (0·00014) is small compared to the linear term (0·0032). Therefore the variation of c/a is linear rather than parabolic. Annapurna and Reddy (1986)

worked on $CuGaSe_2$ and $CuGaTe_2$ solid-solutions in the form of single crystal grown by the vertical Bridgman technique. They also found that the parabolic term was negligibly small. In our result Δ was small and negative, which indicated built-in dilation ($c > 2a$) rather than compression (Shay and Wernick 1975) as is the usual case.

5. Conclusion

Spray pyrolysis is a successful technique for growing thin films of $CuInSe_{2(1-X)}S_{2X}$. X-ray results indicate that films of all compositions have a chalcopyrite structure. Variation of band gap with composition parameter X is linear and not parabolic. Lattice parameters a and c also vary linearly with composition parameter X. Tetragonal distortion is small and negative for all values of X indicating dilation ($c > 2a$) rather than compression. Our values of tetragonal distortion do not follow the hypothetical relation proposed by Phillips (1974).

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