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Electrical properties of chemically prepared nonstoichiometric $CuIn(S,Se)_2$ thin films

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Abstract. Polycrystalline thin films of copper indium sulphoselenide [$CuIn(S,Se)_2$] were deposited on glass substrate by chemical bath deposition technique. The deposition parameters such as pH, temperature and time were optimized. A set of films having different elemental compositions was prepared by varying Cu/In ratio from 1·87–12·15. The films were characterized by X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDAX). The chemical composition of the $CuIn(S,Se)_2$ was found to be nonstoichiometric. The d.c. conductivities of the films were studied below and near room temperature. The thermo-electric power of the films was also measured and type of semiconductivity was ascertained.

Keywords. $CuIn(S,Se)_2$; thin films; chemical bath deposition technique; d.c. conductivity; thermoelectric power.

1. Introduction

$CuIn(S,Se)_2$ abbreviated as (CISS) is an interesting material for the fabrication of thin film solar cells due to its high absorption coefficient, suitable band gap and good stability. To fabricate CISS based heterojunction thin film, solar cell is a recent research and development area for higher efficiency solar cells.

All the thin film deposition techniques used for the fabrication of high efficiency (CISS) compound based cells are very expensive and require sophisticated instruments. In some deposition techniques, H_2Se and H_2S vapours are used as source materials for selenium and sulphur, which are poisonous gases.

A number of thin film growth technologies such as sulfurization and selenization (Ohashi *et al* 1998), two-step growth (Bekker *et al* 2003), co-sputtering and thermal diffusion (Adurodija *et al* 1999) and one-step electrodeposition (Kuranouchi and Nakazawa 1998) have been investigated for the synthesis of CISS thin film compounds. Among all the deposition techniques, chemical bath deposition (CBD) is a well known, simpler, and capable of producing large area fabrication technique at low cost. In CBD technique, wastage of material is minimum and there is no need to handle poisonous gases like H_2Se and H_2S. Chavan and Sharma (2006) reported the preparation procedure of CISS films by chemical bath deposition technique. Efforts are made, in the present article, to synthesize $CuIn(S,Se)_2$ thin films of various chemical compositions to optimize the parameters for uniform deposition of films. The effect of at % of Cu and In in CISS on electrical properties are presented.

2. Experimental

The starting materials used were $CuCl_2{\cdot}2H_2O$, $InCl_3$, Na_2SO_3, Se powder and NH_2–CS–NH_2 (thiourea). Triethanolamine (TEA) was used as a complexing agent. Ammonium hydroxide solution was used to adjust pH of the reaction mixture. All the chemicals used were of AR grade. Good quality films were obtained for optimized time, temperature of deposition and pH of the solution, of 60 min, 60°C and 10, respectively.

The process involved the reaction of Cu^+, In^{3+}, S^{2-} and Se^{2-} ions in deionized water solution. The tetraamine copper $[Cu(NH_3)_4^{2+}]$ was mixed with complex ion of indium–citrate. To this solution TEA was added. A mixture of NH_2–CS–NH_2 and Na_2SeSO_3 was added to this solution in which, Na_2SeSO_3 yielded Se^{2-} and SO_3^{2-} ions. There existed the possibility of reduction of Cu(II) to Cu(I) (Vogel 1978; Garcia *et al* 1999) due to the presence of excess sodium sulphite. The temperature of solution was held at 60°C for 1 h and uniform films of $CuIn(S,Se)_2$ were obtained on glass substrates. Films were annealed in vacuum at 350°C for 20 min. Six samples denoted by samples 1–6 were selected for varying compositions.

Structural characterization of the films was carried out with RIGAKU X-ray diffractometer using Cu$K\alpha$ radiation with wavelength, 1·5418 Å. Elemental analyses of the film were carried out with an EDAX spectrometer. Low

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temperature conductivity measurements were done down to ~80 K employing Keithley 617 programmable electrometer for resistance measurement and a Lakeshore DRC-93 CA controller for temperature control. Electrical conductivity of thin films at high temperature was measured by using d.c. two-probe method in the temperature range 313–423 K. The thermo-electric power (TEP) was measured to decide the type of semiconductivity.

3. Results

3.1 *Structural analysis*

Figure 1 shows diffractogram of sample 6, in the 2θ range of 20–80°. The XRD pattern reveals that a CISS film is polycrystalline in nature. The planes (112), (200), (004), (220), (204) indicate the chalcopyrite structure of the CISS material. In addition to CISS, other phases such as Cu_2S, CuS, Cu_2Se and $CuInSe_2$ are also present. The peak ($\bar{5}33$) shows the presence of binary phase of Cu_2S materials. The peak (703) shows the presence of binary phase of Cu_2Se materials. The peaks (400) and (212) corresponds to $CuInSe_2$ and CuS, respectively.

3.2 *Elemental analysis by EDAX*

The quantitative elemental analysis of the as-prepared films was carried out at room temperature. Table 1 shows the elemental composition of the films from EDAX. Theoretically expected stoichiometric composition of $CuIn(S,Se)_2$ (in terms of at.%) is: Cu = 25%, In = 25%, Se = 25%, S = 25%. It is clear from table 1 that the films are approximately stoichiometric in nature. The results indicate that in addition to $CuIn(S,Se)_2$ other phases such as Cu_2S, CuS, Cu_2Se and $CuInSe_2$ may also be present. Further, at.% of In and S goes on increasing, while at % of Cu and Se goes on decreasing.

3.3 *Electrical conductivity and activation energy*

Figures 2(a) and (b) show logarithmic conductivity ($\log \sigma$) vs inverse of temperature ($1000/T$) for the as prepared samples in the lower temperature range 90–300 K. The conductivity of samples 1 and 2 decreases with increase in temperature, indicating metallic nature of the films. This observation is in line with the larger Cu/In ratios of 12·15 and 10·04, respectively. However, the other four samples, wherein the Cu/In ratios decrease as 5·89, 4·30, 3·02 and 1·87, show increase in conductivity with temperature indicating that the materials become less conducting, minimum being sample 6 with Cu/In = 1·87. The activation energies obtained from these films are given in table 2, which shows decreasing activation energy with increasing Cu/In ratio as represented in figures 3(a) and (b), respectively for low (90–300 K) and high (313–423 K) temperatures.

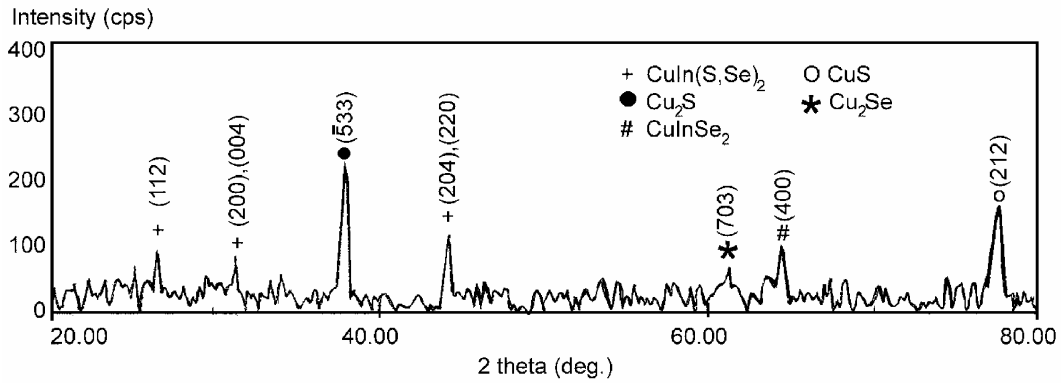

Figure 1. XRD pattern of sample 6.

Table 1. Elemental composition of $CuIn(S,Se)_2$ films.

Sample no.	Cu (at%)	In (at%)	S (at%)	Se (at%)	Cu/In (at%)	S/Se (at%)
1	53·71	4·42	6·52	35·35	12·15	0·184
2	50·30	5·01	6·85	37·85	10·04	0·180
3	47·53	8·07	7·36	37·04	5·89	0·198
4	47·76	11·10	11·51	29·64	4·30	0·388
5	44·05	14·60	17·95	23·40	3·02	0·767
6	36·91	19·77	17·60	25·72	1·87	0·684

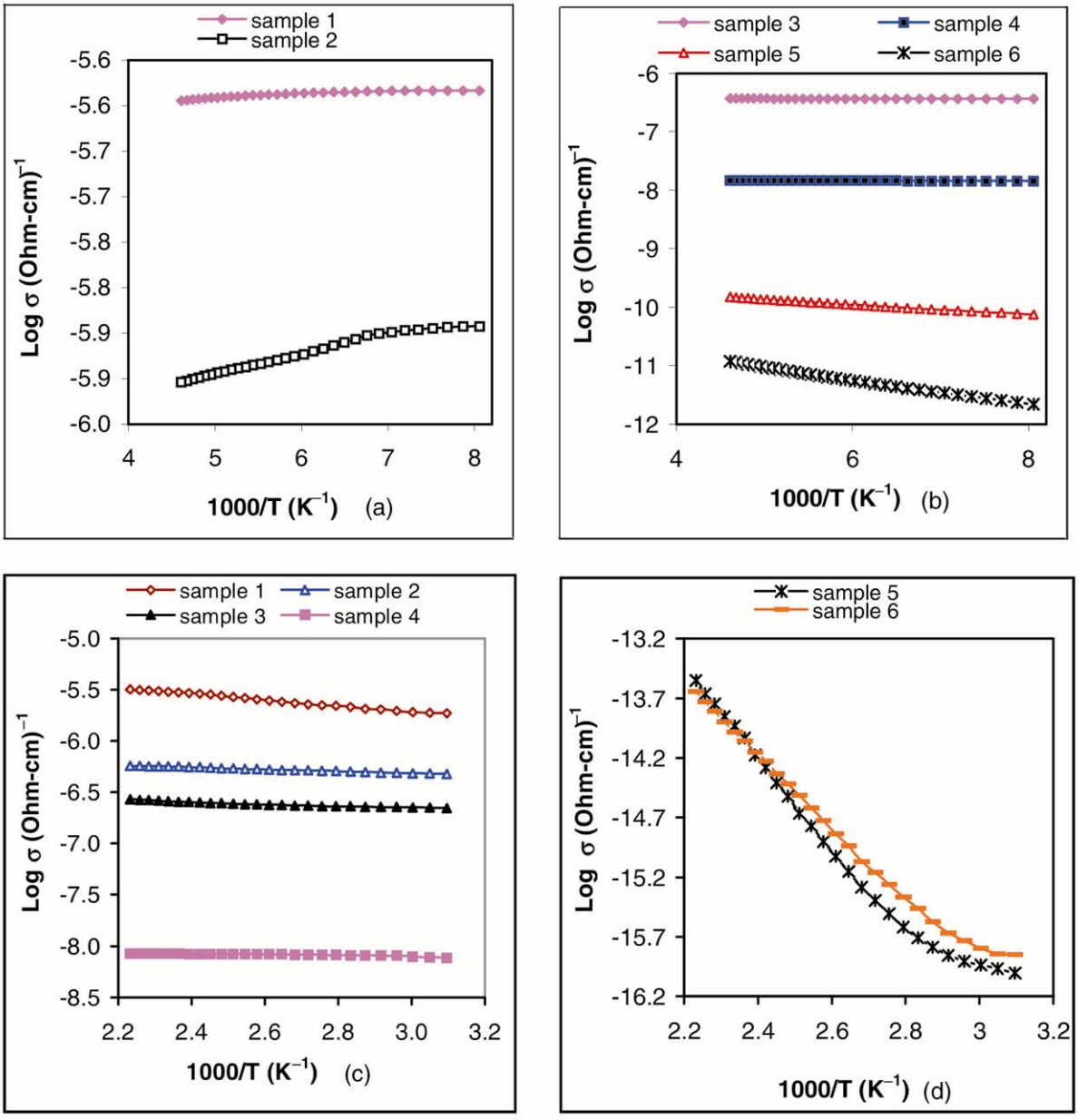

Figure 2. Logarithmic electrical conductivity vs temperature (1000/*T*): (**a**)–(**b**) low temperature (90–300 K) variation and (**c**)–(**d**) high temperature (313–423 K) variation.

Figures 2(c) and (d) show logarithm of electrical conductivity (log σ) vs inverse of temperature (1000/*T*) for the six samples in the higher temperature range 313–423 K. All the six samples, wherein the ratios decrease as 12·15, 10·04, 5·89, 4·30, 3·02 and 1·87, show increasing conductivity with temperature. It is also clear that the materials become less conducting, minimum being sample 6 with Cu/In = 1·87. The activation energies obtained from these films are given in table 2, which shows decreasing trend in activation energy with increasing Cu/In ratio.

In both the low and high temperature regions, the conductivity is larger for the films with high Cu/In ratio. In short, higher Cu concentration in the film leads to better conductivity and reduced activation energy.

3.4 *Thermoelectric power*

In a semiconductor, temperature gradient yields the thermoelectric effect, in which phonons travel preferentially from the hot end to cold end due to electron–phonon interactions. During TEP measurements, thermal gradient established changes the density of charged defect state by capturing electrons and holes. The motion of the electrons and holes can take place through the process of diffusion.

Table 2. Dependence of activation energy on Cu/In ratio.

Sample	Cu (at%)/ In (at%)	Activation energy (at low temp.) (eV)	Activation energy (at high temp) (eV)	Conductivity (σ) $(\Omega\text{-cm})^{-1}$ (at 384 K)	TEP (S) (μV/K) (at 384 K)
1	12·15	0·0030	0·018	$2{\cdot}47 \times 10^{-6}$	–6·05
2	10·04	0·0036	0·019	$2{\cdot}38 \times 10^{-7}$	–2·99
3	5·89	0·0057	0·052	$5{\cdot}24 \times 10^{-7}$	–0·95
4	4·30	0·0170	0·252	$8{\cdot}30 \times 10^{-9}$	0·4
5	3·02	0·0201	0·615	$1{\cdot}45 \times 10^{-15}$	4·06
6	1·87	0·042	0·743	$9{\cdot}39 \times 10^{-16}$	4·91

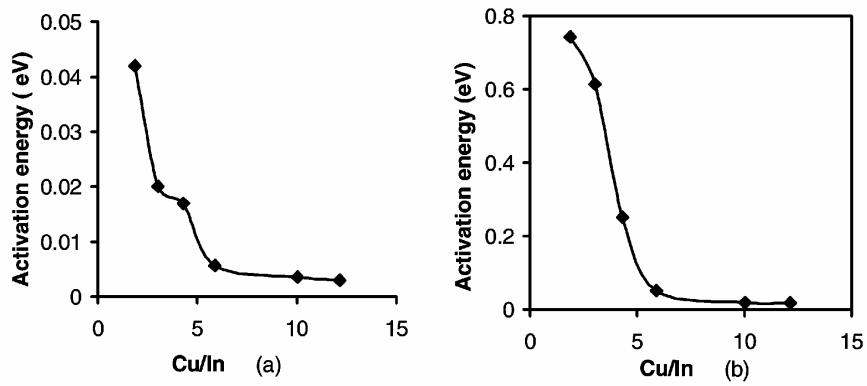

Figure 3. Variation of activation energy with Cu/In ratio in the temperature range: (**a**) 90–300 K and (**b**) 313–423 K.

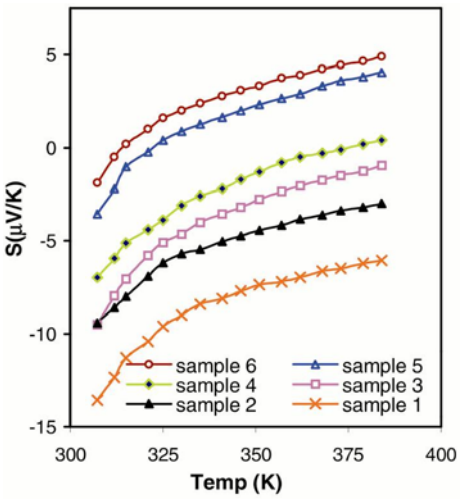

Figure 4. Temperature dependence of thermoelectric power of various $CuIn(S,Se)_2$ samples.

Figure 4 shows thermoelectric power (S) vs temperature curves for different compositions of CISS. It is clear from the figure that S goes on increasing with temperature for all samples. TEP is negative for samples 1–4 during the temperature range of 307–384 K indicating n-type conductivity (Mahdjuri 1975). This type of behaviour is for the samples with Cu/In ratio > 4·3. For the samples 5 and 6, the Cu/In ratio is < 3·02. These samples behave differently from samples 1–4. The samples have negative TEP up to 320 K, indicating n-type nature. At temperature >320 K, the TEP values are positive indicating p-type nature. This could be attributed to the temperature dependent type of conductivity.

4. Discussion

The $CuIn(S,Se)_2$ was synthesized using chemical bath deposition technique. The following chemical reactions represent the synthesis process:

(a) There exist the possibility of reduction of Cu(II) to Cu(I) (Vogel 1978; Garcia *et al* 1999) due to the presence of excess sodium sulphite,

$$SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + H_2O + 2e^-,$$

$$Cu^{2+} + e^- \rightarrow Cu^{+1}. \quad (1)$$

(b) Copper salt reacts with the reagent (triethanolamine) to form the metal complex (Chavan and Sharma 2005)

$$Cu^{1+} + n(TEA) \rightarrow [Cu(TEA)n]^{1+}. \quad (2)$$

(c) Formation of In^{3+} ions (Sharma 1991) form the complex with citric acid as follows

$$InCl_3 + C_6H_8O_7 \rightarrow In(C_6H_5O_7) + 3HCl.$$
(In-citrate)

By addition of TEA in indium citrate complex ions, the solution is basic and indium forms complex with TEA as follows:

$$In(C_6H_5O_7) + n(TEA) \rightarrow [In(TEA)n]^{3+} + C_6H_5O_7. \quad (3)$$

(d) In the alkaline medium, the selenide ions are released as follows (Lokhande *et al* 1999; Sutrave *et al* 2000):

$$Na_2SeSO_3 + OH^- \rightarrow HSe^- + Na_2SO_4,$$

$$HSe^- + OH^- \rightarrow Se^{2-} + H_2O. \quad (4)$$

(e) The sulphide ions are released due to decomposition of thiourea in an alkaline medium. It is described by the following chemical reactions (Nair *et al* 1987)

$$SC(NH_2)_2 + 3OH^- \rightarrow 2NH_3 + CO_3^{2-} + HS^-,$$

$$HS^- + OH^- \rightarrow S^{2-} + H_2O. \quad (5)$$

From (2)–(5), we can write

$$[Cu(TEA)n]^{+1} + [In\ (TEA)n]^{3+} + 2\ Se^{2-} + 2\ S^{2-} + 2H_2O \xrightarrow[60^\circ C]{pH\,10} CuIn(S,Se)_2 + 2n\text{TEA} + \text{waste product}.$$

The electrical properties of the as prepared films such as variation of (i) electrical conductivity with temperature, (ii) activation energy with change of Cu/In ratio, and (iii) thermoelectric power with temperature were studied. The increase of electrical conductivity with temperature reveals the semiconducting nature of $CuIn(S,Se)_2$ films which may be attributed to the higher amount of copper in a particular compound. Decrease of activation energy with increase of Cu/In ratios could be attributed to higher conductivity of films.

5. Conclusions

Copper indium sulphoselenide films were deposited on to glass substrate by a simple chemical bath deposition technique. The films obtained were uniform and had good adherence to the substrate. The EDAX data indicated that films were nonstoichiometric. For both low and high temperature regions, the conductivity was higher with high Cu/In ratio. Also, higher Cu concentration in the film leads to reduced activation energy. These films showed metallic nature for higher Cu/In ratio and semiconducting nature for lower Cu/In ratio. TEP was observed to be increased with increase in temperature. The conduction through the samples having lower Cu/In ratio is due to hole, while the conduction through the samples having higher Cu/In ratio is due to electrons.

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