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Structural and optical characterization of CuInSe₂ films deposited by hot wall vacuum evaporation method

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Abstract

Copper indium diselenide (CuInSe₂) compound was prepared by direct reaction of high-purity elemental copper, indium and selenium. CuInSe₂ thin films were deposited onto well-cleaned glass substrates by a hot wall deposition technique using quartz tubes of different lengths (0.05, 0.07, 0.09, 0.11 and 0.13 m). X-ray diffraction studies revealed that all the deposited films are polycrystalline in nature and exhibit chalcopyrite structure. The crystallites were found to have a preferred orientation along the (1 1 2) direction. Micro-structural parameters of the films such as grain size, dislocation density, tetragonal distortion and strain have been determined. The grain sizes in the films were in the range of 65–250 nm. As the tube length increases up to 0.11 m the grain size in the deposited films increases, but the strain decreases. The film deposited using the 0.13 m long tube has smaller grain size and more strain. CuInSe₂ thin films coated using a tube length of 0.11 m were found to be highly crystalline when compared to the films coated using other tube lengths; it has also been found that films possess the same composition (Cu/In = 1.015) as that of the bulk. Scanning electron microscope analysis indicates that the films are polycrystalline in nature. Structural parameters of CuInSe₂ thin films deposited under higher substrate temperatures were also studied and the results are discussed. The optical absorption coefficient of CuInSe₂ thin films has been estimated as 10⁴ cm⁻¹ (around 1050 nm). The direct band gap of CuInSe₂ thin films was also determined to be between 1.018 and 0.998 eV.

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Keywords: CuInSe₂; Thin films; Structure; Composition; Optical; Hot-wall deposition

1. Introduction

The ternary (I–III–VI₂) semiconductor CuInSe₂ (CIS) has become one of the leading materials for large-scale thin-film solar cell applications because of its direct band gap, high absorption coefficient and good thermal stability. CIS has received considerable attention as one of the most promising materials for second-generation solar cells. Currently, efficiencies above 19% have been achieved [1,2]. No evidence for long- or short-term device degradation, as has been found in a-Si devices, is observed in the cells of CIS. In the past, CIS thin films have been prepared

using different techniques such as co-evaporation [3], molecular deposition [4], sputtering [5], selenization [6], chemical bath deposition [7] and close space-vapor transport technique [8]. Among the different techniques available for the deposition of thin films, hot wall epitaxy has become a popular technique, since it is a relatively simple technique, which can be used to prepare high-quality epitaxial thin films with smooth surfaces under conditions very close to thermodynamic equilibrium. It is the technique that has contributed significantly to the preparation of epitaxial films of congruently evaporating compound semiconductors with bulk-like properties [9]. Schikora et al. [10] have claimed that hot wall deposited CdTe films on GaAs substrates show superior luminescence properties when compared to MBE and MOCVD films. In the present study CIS thin films have

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been deposited using a hot wall deposition technique. A systematic study has been made on CIS thin films deposited using different tube lengths onto glass substrates to optimize the tube length to obtain stoichiometric films. Structural and compositional studies have been carried out on all the deposited films and the optimum tube length has been identified. Using the optimized tube length, CIS films have been prepared on glass substrates at different substrate temperatures and their structural properties have been studied. The nature of transition and optical band gap values of CIS thin films have been determined from the transmittance spectra.

2. Experimental technique

CIS has been synthesized by direct reaction of high-purity (99.999%) elemental copper, indium and selenium. Stoichiometric amounts of the elements Cu, In and Se were placed in a quartz ampoule that was evacuated to a pressure of 10^{-5} Torr and then sealed. The ampoule was heated gradually at the rate of 100 K per hour in steps up to 1430 K and it was maintained at this temperature for 24 h and then allowed to cool slowly to room temperature. During the course of heating and cooling, the quartz ampoule was rotated continuously to ensure homogeneity of the molten mixture. The CIS material isolated from this reaction served as the starting material for film deposition onto glass substrates by a hot wall deposition technique. The schematic diagram of the hot wall experimental set-up is shown in Fig. 1. The main feature of the system is the heated linear quartz tube, which serves to enclose and direct the vapor from source to substrate. Kanthal wire wound closely along the length of the quartz tube is used to heat the wall of the quartz tube. Three independent heater

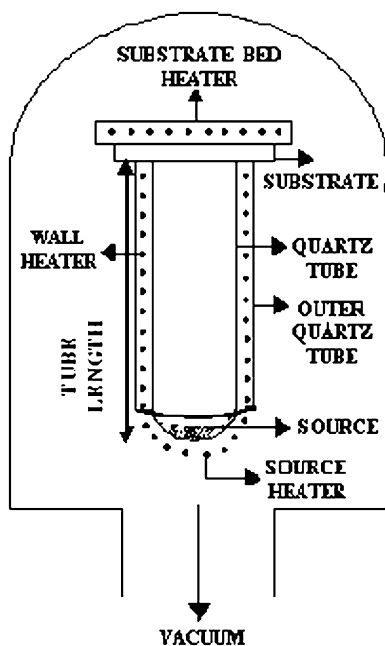


Fig. 1. Schematic diagram of hot wall deposition set-up.

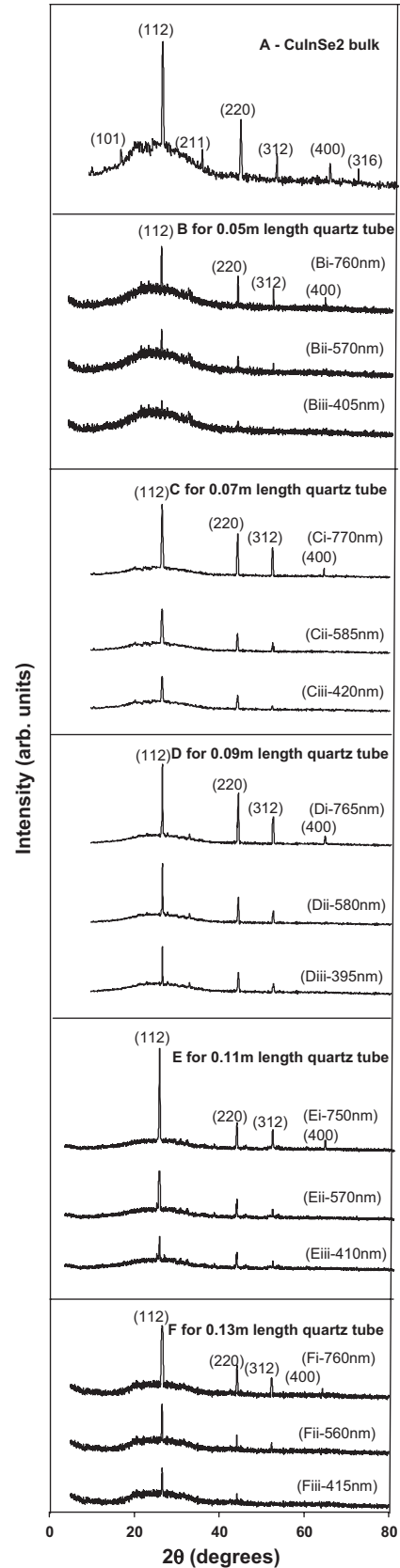


Fig. 2. X-ray diffraction pattern of CuInSe_2 (A) bulk and thin films of various thicknesses deposited by using quartz tube of lengths (B) $l = 0.05$ m, (C) $l = 0.07$ m, (D) $l = 0.09$ m, (E) $l = 0.11$ m and (F) $l = 0.13$ m.

coils were used to heat the source, wall of the tube and the substrate. The substrate was held at a distance of less than 1 mm exactly above the open end of the quartz tube and acted almost as a lid, closing the tube with the help of a substrate holder/heater assembly. The quartz tube was charged with the prepared CIS compound and the whole arrangement was placed inside the vacuum chamber in which a pressure of 10^{-5} Torr was achieved prior to the growth of the film. CIS thin films have been deposited using 10 mm diameter quartz tubes of lengths 0.05, 0.07, 0.09, 0.11 and 0.13 m, with the source and wall temperatures around 1370 K. Due to radiation of heat from the hot wall, the substrate temperature was found to increase by 70 K under normal coating conditions. The thicknesses of the films have been determined using a gravimetric technique and confirmed by multiple beam interferometer technique [11]. The structure of the films has been studied by X-ray diffractometry (Model Philips PW 3710 with CuK_α radiation). The surface topography and composition of the deposited films have been determined using scanning electron microscopy (SEM) in conjunction with energy dispersive X-ray analysis (EDX) (Model 7060 Oxford Instruments, Cambridge). Optical transmission spectra were acquired from a UV-VIS-NIR Spectrophotometer (Model JASCO V-570) in the wavelength range 500–2500 nm and subsequently analyzed.

3. Results and discussion

3.1. Structural characterization

The X-ray diffractograms of the prepared bulk CIS compound and its thin films deposited using a quartz tube of different lengths are shown in Fig. 2. The presence of sharp peaks in the X-ray diffractogram shows that the prepared CIS compound is polycrystalline in nature. The

CIS compound is found to exhibit a chalcopyrite structure with a preferred orientation along certain crystallographic planes which have been identified as (1 0 1), (1 1 2), (2 1 1), (2 2 0), (3 1 2), (4 0 0) and (3 1 6). The same chalcopyrite structure for CIS compound is equivalent to that obtained by Senthil et al. [12]. The lattice parameter values a and c , in the bulk compound have been found to be 5.784 and 11.617 Å, respectively, and they are in good agreement with

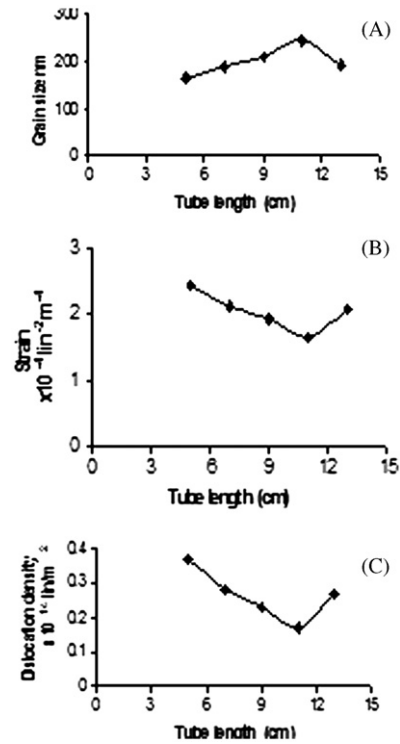


Fig. 3. Variation of (A) grain size, (B) strain and (C) dislocation density with the quartz tube length in films having thickness around 760 nm.

Table 1

Structural parameters for CuInSe_2 thin films of different thickness deposited using different quartz tube lengths

Tube length (m)	Film thickness (nm)	Lattice parameter		c/a (ratio)	Tetragonal distortion $2-c/a$	Grain size D (nm)	Dislocation density ($\times 10^{14} \text{ lin}^{-2} \text{ m}^{-2}$)	Strain ε ($\times 10^{-4} \text{ lin}^{-2} \text{ m}^{-4}$)
		a (Å)	c (Å)					
0.05	405	5.798	11.534	1.9893	0.0107	67.34	2.205	5.983
	570	5.799	11.528	1.9879	0.0121	102.71	0.948	3.392
	760	5.798	11.531	1.9887	0.0113	164.69	0.369	2.446
0.07	420	5.791	11.548	1.9941	0.0059	73.56	1.898	5.475
	585	5.789	11.556	1.9962	0.0038	124.64	0.644	3.232
	770	5.788	11.564	1.9979	0.0021	189.31	0.279	2.128
0.09	395	5.785	11.597	2.0046	-0.0046	79.82	1.569	4.752
	580	5.786	11.618	2.0079	-0.0079	150.98	0.438	2.668
	765	5.779	11.590	2.0055	-0.0055	208.76	0.229	1.929
0.11	410	5.779	11.623	2.0112	-0.0112	89.37	1.252	4.507
	570	5.780	11.621	2.0105	-0.0105	162.75	0.378	2.475
	750	5.785	11.613	2.0074	-0.0074	243.68	0.168	1.653
0.13	415	5.778	11.635	2.0136	-0.0136	77.46	1.667	5.199
	560	5.765	11.638	2.0187	-0.0187	140.83	0.504	2.859
	760	5.754	11.641	2.0231	-0.0231	193.51	0.267	2.081

the American Society for Testing and Materials (ASTM) values ($a = 5.782 \text{ \AA}$ and $c = 11.619 \text{ \AA}$).

All the deposited CIS films are found to be polycrystalline in nature and exhibit the chalcopyrite structure with orientation along (1 1 2), (2 2 0) and (3 1 2) directions. The (4 0 0) orientation is seen only in thicker films. The microstructural parameters of the deposited CIS films, like lattice parameter (a , c), c/a ratio, tetragonal distortion, grain size, dislocation density and strain have been evaluated [13,14] and are shown in Table 1. It is observed that the grain size initially increases but the strain and dislocation density decrease with the increase of film thickness for the CIS films deposited using different tube lengths. A similar dependence of grain size, strain and dislocation density has been reported by Dhanam et al. [7] for CBD CIS films. The grain size, dislocation density and strain were found to be dependent on tube length. The variation of grain size, strain and dislocation density with tube length is shown in Fig. 3. It is observed that the grain size increases with tube length and reaches a maximum for a tube of length 0.11 m and then decreases. The strain and dislocation density are found to decrease and reach a minimum for a tube of length 0.11 m and then increase. CIS films deposited using the 0.11 m length tube are found to have a large grain size, with less strain and dislocation density.

The EDX pattern of CIS compound and the corresponding film deposited using the 0.11 m length tube are shown in Fig. 4(A) and (B) respectively. It is found that the elemental composition in the bulk is nearly identical to that

seen in the film deposited by using a tube length of 0.11 m. The chemical compositions of the constituents in the CIS films deposited using different tube lengths are shown in Table 2. Films deposited using tubes of lengths 0.05, 0.07 and 0.09 m are found to have a Cu/In ratio less than one. With these tube lengths, elemental compositions markedly deviate from the stoichiometric composition. This non-stoichiometric composition observed in films deposited using smaller tube lengths may be attributed to direct vapor transport of species from the source without making sufficient wall collision to attain thermal equilibrium. Also the molecular flux distribution may not be uniform for small tube lengths. For thermal equilibrium, the direct vapor phase transport of molecules should be minimized so that vapor species are able to attain thermal equilibrium with the heated wall before they reach the substrate. For larger tube lengths, the number of wall collisions suffered by the molecules is sufficient for the molecules to attain thermal equilibrium before they reach the substrate and diffusion is minimized. The gas phase flux density distribution at the substrate may also be uniform for larger tube lengths. However, the composition analysis data, which are given in Table 2, indicate that the Cu/In ratio is less than one for films deposited using a tube of length 0.13 m. This may be due to the increase in the number of species arriving at the substrate after colliding with the hot wall for this longer tube length.

From Fig. 5, it is clear that the Cu/In ratio increases as the tube length increases and reaches a maximum for a

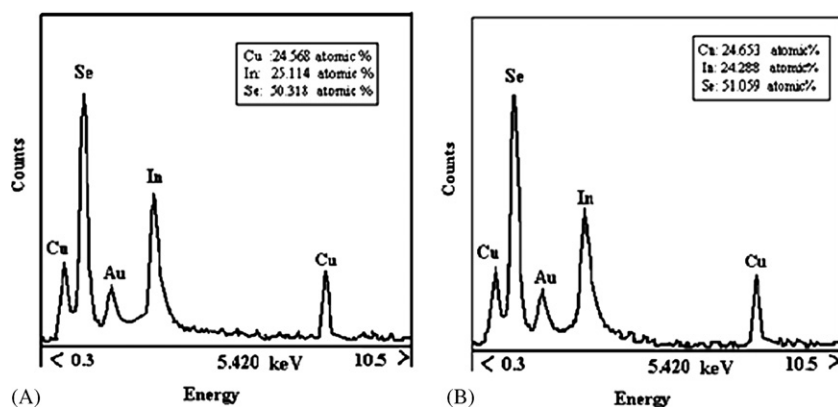


Fig. 4. (A) EDAX pattern of CuInSe_2 bulk and (B) EDAX pattern of CuInSe_2 thin films deposited using the optimized quartz tube of length 0.11 m.

Table 2
Elemental composition in CuInSe_2 thin films deposited using different lengths of the quartz tube

Tube length (m)	Film thickness (nm)	Atomic percentage in the CuInSe_2 thin films			Cu/In ratio	Grain size (nm)
		Copper (%)	Indium (%)	Selenium (%)		
0.05	760	11.326	28.938	59.736	0.391	164.69
0.07	770	14.070	30.732	55.198	0.458	189.31
0.09	765	21.645	23.986	54.369	0.902	208.76
0.11	750	24.653	24.288	51.059	1.015	243.68
0.13	760	20.473	27.618	50.909	0.741	193.51

tube of length 0.11 m followed by a decrease. The increase of copper content increases the grain size, in turn yielding good polycrystallites [15,16]. All these results show that the 0.11 m length tube yields films with large grains, less strain and dislocation density, good composition, and comparable a and c values. Hence, this tube length could be considered as the optimum length for preparing stoichiometric CIS films by using the hot wall deposition technique. CIS thin films with a Cu/In ratio greater than one have been reported by Menna et al. [17] as suitable for high-efficiency devices. The films prepared in the present study possess this value.

The scanning electron microscope images of the CIS bulk material and the resulting thin film coated using the 0.11 m length tube are shown in Fig. 6(A) and (B), respectively. The SEM micrograph confirms the crystalline nature of the film.

The X-ray diffraction pattern of the CIS films deposited at different substrate temperatures using the tube of optimum length 0.11 m is shown in Fig. 7. The films deposited at temperatures of 423, 523 and 673 K are found to exhibit a crystalline structure with orientation of the crystallites along (112), (220) and (312) directions. As the substrate temperature is increased, the films are found to show a highly preferred orientation along the (112) direction in accordance with that characteristic of a single crystal. Since the strain and dislocation density are manifestations of the dislocation network in the films, the

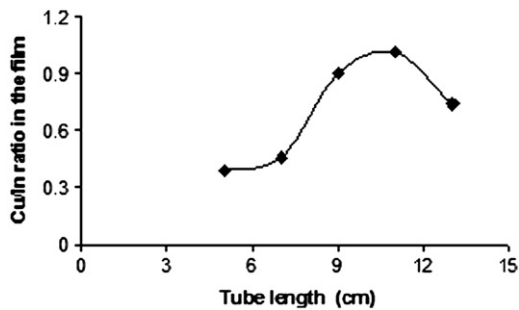


Fig. 5. Variation of Cu/In ratio with the quartz tube length for the films having thickness around 760 nm.

decrease in both these parameters indicates the formation of high quality films. The presence of (112), (220) and (312) diffraction peaks confirm the chalcopyrite structure [4,18].

3.2. Optical properties

The transmittance spectra of the 0.11 m hot wall deposited thin films with two representative thicknesses (570 and 750 nm) in the wavelength range 500–2500 nm are shown in Fig. 8. The inset is a Tauc's plot of the square of absorption coefficient as a function of energy from which the band gap energy was determined. For all the films there is a rapid decrease in the transmittance value near the absorption edge. The optical absorption coefficient reaches 10^4 cm^{-1} near the optical absorption edge. The calculated

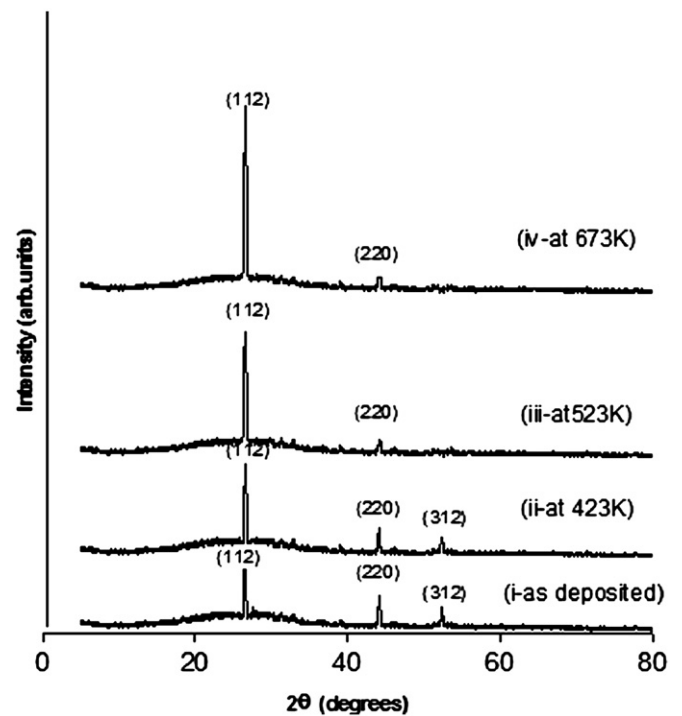


Fig. 7. X-ray diffraction pattern of CuInSe_2 thin films deposited at various substrate temperatures using an optimized quartz tube of length 0.11 m.

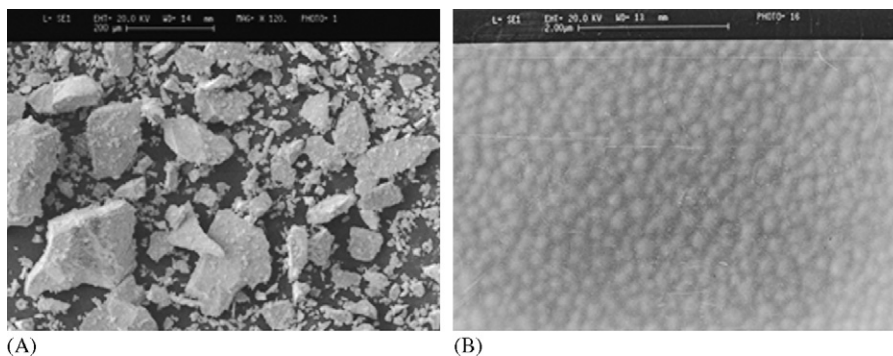


Fig. 6. (A) SEM micrograph of CuInSe_2 bulk powder and (B) SEM micrograph of CuInSe_2 thin film deposited using an optimized quartz tube of length 0.11 m.

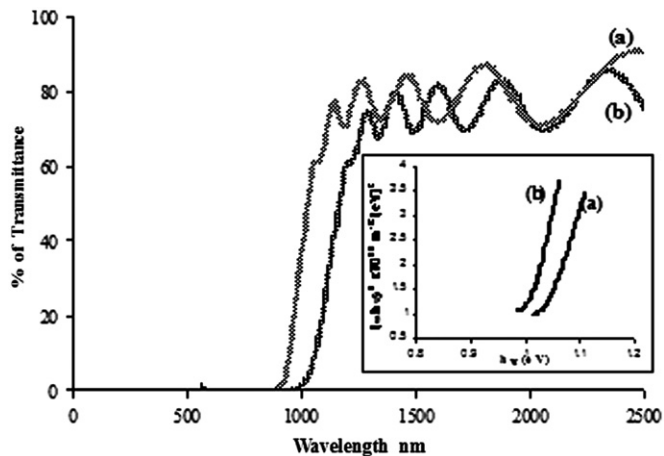


Fig. 8. The transmittance spectra of hot wall deposited CuInSe₂ thin films with films of thicknesses (a) 570 nm and (b) 750 nm. Inset is the plot of $(\alpha hv)^2$ versus $h\nu$ for CuInSe₂ thin films of thicknesses (a) 570 nm and (b) 750 nm.

absorption coefficient of these CIS thin films is in good agreement with earlier reported studies [19–21]. The linear dependence of $(\alpha hv)^2$ with $h\nu$ near the band edge confirms that the CIS is a direct band gap material. The optical bandgaps of CIS thin films with thicknesses 570 and 750 nm were determined as 1.018 and 0.998 eV, respectively. This range is in good agreement with other authors [22,23]. It is observed that as the thickness increases, the band gap decreases. This may be attributed to the larger grain size and decreased strain in the thicker film.

4. Summary and conclusion

CIS films have been deposited by a hot wall deposition technique using quartz tubes of different lengths. The microstructural parameters, viz., lattice constants, grain size, dislocation density and strain, have been calculated. The compositions of the films have been determined from EDX. The optimum tube length for depositing stoichiometric CIS films with large grain size, less strain, less dislocation density and comparable composition to the bulk compound material has been determined to be 0.11 m. As the substrate temperature is increased, the films are found to show a highly preferred orientation along the (1 1 2) direction. The direct band gap values of CIS thin films were determined from the transmission spectra to range from 1.018 eV to 0.998 eV depending on film thickness.

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