

INFLUENCE OF SUBSTRATE TEMPERATURE ON THE STRUCTURAL AND OPTICAL PROPERTIES OF $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ FILMS

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Thin films of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ were prepared on glass substrates held at temperatures in the range 473 – 748 K, by flash evaporation technique. The effect of substrate temperature on the chemical composition, structure, surface morphology and optical properties of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films was systematically investigated. The $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films deposited at a substrate temperature of 693 K were single phase, polycrystalline with mean grain size around 500 nm and the fundamental optical band gap of 1.14 eV.

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1. Introduction

The utilization of several I-III-VI₂ chalcopyrite semiconductors has been reported in the literature for application in thin film solar cells [1–4]. The family of the chalcopyrite semiconductors offer numerous possibilities of obtaining absorber materials of desired properties which can be effectively used in the fabrication of high efficiency and low cost solar cells. Thin films of copper based chalcopyrite absorber materials are attracting the attention of many researchers because of their favourable optoelectronic properties and good stability makes them suitable for photovoltaic and optoelectronic device applications. These compounds are particularly suitable for making p-n heterojunctions with the II-VI compounds. Copper indium diselenide (CuInSe_2) and silver indium diselenide (AgInSe_2) ternary compounds are direct band gap semiconductors which crystallizes in the chalcopyrite structure. These compounds have nearest electronic and chemical analogies of A^{II}B^{VI} binary compounds [1]. CuInSe_2 has an optical band gap of 1.04 eV and AgInSe_2 optical band gap of 1.24 eV which have already proven their suitability for absorber layers in fabricating thin film heterojunction solar cells [5–9] apart from the field induced transistors [10] and p-n junction diodes [11].

Studies on the quaternary compound, $\text{Cu}_x\text{Ag}_{1-x}\text{InSe}_2$ films as an absorber material for heterojunction solar cells are still more attractive, since they allow tailoring of the optical band gap, lattice parameter and other physical properties. By gradually substituting copper with silver, the optical band gap can be increased from 1.04 eV to 1.24 eV. Very little work has been reported on the bulk properties of $\text{Cu}_x\text{Ag}_{1-x}\text{InSe}_2$ [12–18]. Gremenok et al [19] reported the growth and characterization of $\text{Cu}_x\text{Ag}_{1-x}\text{InSe}_2$ ($x = 0$ to 1.0) thin films prepared by pulsed laser deposition. A better understanding of structural, electrical and optical properties is essential for optimizing these films for solar cell fabrication. The preparation of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films by flash evaporation technique and their electrical properties [20] and photoconductive response [21] were reported earlier. In this investigation, an attempt has been made in the deposition of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films by flash evaporation technique and the influence of substrate temperature on the structure was studied by using X-ray diffraction, Atomic Force Microscopy and optical properties using spectrophotometric method.

2. Experimental

Ingots of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ have been prepared using constituent elements of pure copper, silver, indium and selenium (obtained from M/S Johnson Matthey, UK) weighed in stoichiometric ratios in sealed evacuated quartz ampoule held at 1373 K for 48 hours. The ingots were pulverized. $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ thin films were grown on Corning 7059 glass substrates held at temperatures (T_s) in the range 473 – 748 K using the flash evaporation technique in a Balzers BA 510 E high vacuum coating unit in a vacuum of 2×10^{-6} Torr. The evaporant powder was continuously dropped into the molybdenum boat heated held at a temperature of about 1773 K through a Balzers BWF 103 vibratory feeder resulting a rate of deposition of 1 nm / sec of the grown films. The thickness of the films was monitored using a quartz crystal thickness monitor during the deposition. The films were uniform, pinhole free and strongly adherent to the surface of the substrate. $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films were grown under identical conditions by keeping all the deposition parameters constant except the substrate temperature.

Philips computerized Scanning Auger Microprobe system (model SAM PHI 590A) was used for the analysis of the film composition. The system consists of a probe electron beam of diameter 0.2 μm at 3 keV. A Siemens D 5000 thin film X-ray Diffractometer ($\text{Cu K}\alpha$ target with $\lambda = 0.15402$ nm) was used for structural characterization of the films. Atomic Force Microscopy (AFM) Digital Instruments Dimension 3100 Series was used to study the surface morphology of the films. The optical transmittance and reflectance of the films was recorded using U-3400 double beam spectrophotometer.

3. Results and discussion

Chemical composition of the $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films was analyzed using Auger Electron Spectroscopy (AES). The elemental weight percentages of copper, silver, indium and selenium were found to depend critically on the substrate temperature. The films deposited at $T_s < 683$ K contained an excess of selenium and indium, and deficient in silver and copper. This differences may be due to the slight decomposition of the compound and / or differences in the vapour pressures of ($P_{\text{Se}} > P_{\text{In}} > P_{\text{Ag}} > P_{\text{Cu}}$) constituent elements in the quaternary compound [22]. The films formed at $T_s = 683 - 703$ K were found to be nearly stoichiometric [20]. A typical Auger electron spectrum of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ film formed at a substrate temperature of 693 K is shown in Fig. 1. For the near stoichiometric films, the calculated weight percentages (wt.%) of Cu, Ag, In and Se were 9.1, 15.5, 31.8 and 43.6 respectively. The achieved values are comparable with those of the stoichiometric powder (Cu = 8.9 wt.%, Ag = 15.05 wt.%, In = 32.0 wt.% and Se = 44.05 wt.%) within the limits of experimental error of ± 0.5 wt.%.

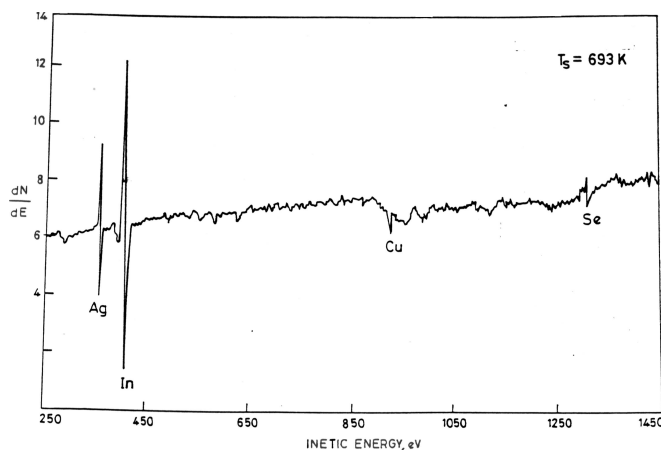


Fig. 1. Auger Electron Spectrum of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ film formed at a substrate temperature of 693 K.

The structure of the films was determined using X-ray diffraction (XRD). The substrate temperature was found to have significant influence on the crystallographic structure and surface morphology of the deposited films. Fig. 2 shows the X-ray diffraction profiles of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films formed at different substrate temperatures. The $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films formed at substrate temperatures < 573 K were amorphous in nature while those prepared at $T_S = 573 - 673$ K were polycrystalline and non-stoichiometric. The films deposited at $T_S = 623$ K were found to contain an additional phase of InSe (Fig. 2a). The films deposited at $T_S = 693$ K (Fig. 2b) were polycrystalline with strong preferred orientation along (112) direction. The X-ray diffraction data revealed that the films formed at $T_S = 683 - 703$ K were single-phase, polycrystalline and nearly stoichiometric. The lattice parameters evaluated were found to be $a = 0.5937$ nm, $c = 1.1633$ nm and $c/a = 1.959$ which are comparable to those reported in the literature [14]. The grain size of the film formed at a substrate temperature of 693 K was evaluated from the full width at half maximum of X-ray diffraction peak of (112) was about 500 nm. The films deposited at a substrate temperature of 723 K were found to contain additional phases of Cu_2Se and Ag_2Se along with the $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ as shown in Fig. 2c.

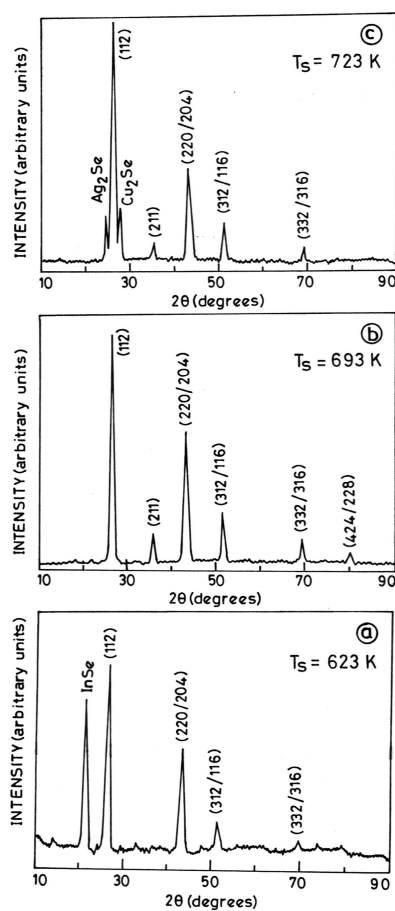


Fig. 2. X-ray diffraction profiles of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films formed at different substrate temperatures : (a) $T_S = 623$ K, (b) $T_S = 693$ K and (c) $T_S = 723$ K.

The morphological characteristics of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films have been studied using Atomic Force Microscopy (AFM) to observe more insight into the microstructure. The surface topographical images recorded for $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films deposited at different substrate temperatures are shown in Fig. 3. The surface morphology of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films deposited at 473 K is shown in Fig. 3a. The microstructural features of these films are characterized by high density columnar structure with low surface roughness. Fine clusters of varying sizes are observed to be distributed uniformly. The root mean square roughness and the average grain size were 2 nm and 150 nm respectively.

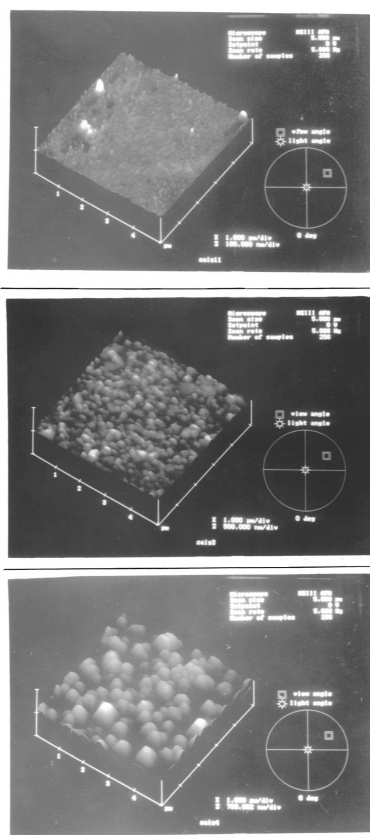


Fig. 3. AFM images of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films formed at different substrate temperatures: (a) $T_S = 473$ K, (b) $T_S = 623$ K and (c) $T_S = 693$ K.

The surface morphological changes were observed in the films deposited at higher substrate temperatures. Fig. 3b represents the AFM picture of the film deposited at 623 K. The surface topography is composed of clusters of varying sizes with irregular shapes. The average grain size and surface roughness were 18 nm and 300 nm respectively. The irregular shape of grains suggest that at low substrate temperatures the kinetic energy is not sufficient for the coalescence of the grains which may led to the presence of additional phases as evident from the XRD analysis. It is evident from the AFM micrographs that the shape of the grains changes with increasing substrate temperature in addition to the grain size. Fig. 3c shows the AFM micrograph of the film deposited at 693 K. The shape of the grains is of square pyramidal type with uniform distribution over the surface. The columnar growth is observed to be perpendicular to the substrate surface. The maximum grain size obtained for these films was about 500 nm.

The temperature dependence of growth and morphology can be explained on the basis of species on the substrate surface as follows. The evaporated atomic or molecular species on the substrate surface acquire a large thermal energy and hence a large mobility when deposited at higher substrate temperatures. This enhances the diffusion distance of the evaporated species. As a result, the collision process initiate the nucleation and enhances the island formation in order to grow continuous film with larger grains. The grain size was found to decrease with increasing substrate temperature beyond 703 K which may be due to the reevaporation of selenium.

The optical transmittance and reflectance of the films were recorded in the wavelength range 300 - 1600 nm. The wavelength dependence of optical transmittance spectra of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films formed at different substrate temperatures are shown in Fig. 4.

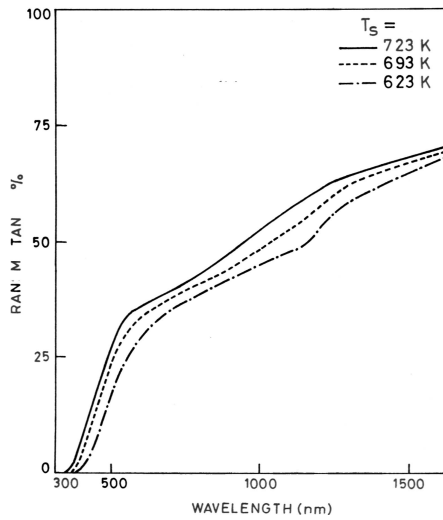


Fig. 4. Optical transmittance spectra of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films formed at different substrate temperatures.

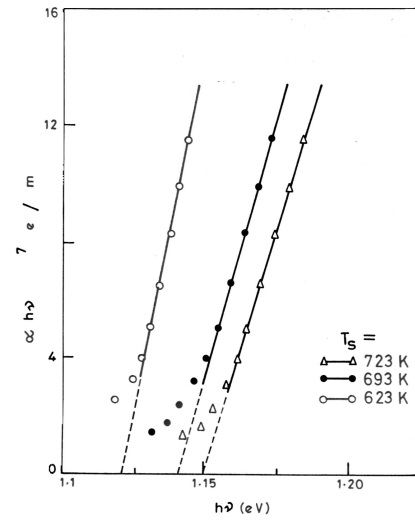


Fig. 5. Plots of $(\alpha h\nu)^2$ versus $h\nu$ of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films formed at different substrate temperatures.

The absorption humps are observed in the optical transmittance spectra. The optical absorption coefficient (α) was evaluated in the photon energy ($h\nu$) < 1.20 eV from the optical transmittance (T) and reflectance (R) data using the relation

$$T = (1-R)^2 \exp(-\alpha t) \quad (1)$$

where t is the film thickness. The dependence of absorption coefficient α with $h\nu$ < 1.20 eV was found to obey the relation

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

for the allowed direct transition from the parabolic valence band to the conduction band, A is an edge width parameter and E_g the fundamental optical band gap. The fundamental optical band gap was evaluated by extrapolation of $(\alpha h\nu)^2$ versus $h\nu$ at $\alpha = 0$. Fig. 5 shows the plots of $(\alpha h\nu)^2$ versus $h\nu$ for the films formed at different substrate temperatures. The fundamental optical band gaps of the films observed were 1.12 eV, 1.14 eV and 1.15 eV corresponds to the films formed at substrate temperatures of 623 K, 693 K and 723 K respectively. The increase of optical band gap with increasing substrate temperature may be attributed to the partial fulfillment of the conduction band by the free carriers and results in the blocking of the lowest states [23], in turn widens the optical band gap which is known as Burstein – Mass shift [24].

The optical band gaps for the films formed at a substrate temperature of 693 K were also evaluated at higher energy range. The achieved optical band gaps of 1.19 eV and 1.45 eV were attributed to the band splittings by crystal-field and spin-orbit effects respectively [1]. These values of optical band gaps are comparable to those of 1.08 eV, 1.14 eV and 1.35 eV reported in films prepared by pulsed laser deposition [19].

4. Conclusions

Thin films of $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ were deposited onto glass substrates held at temperatures in the range 473 - 723 K employing flash evaporation technique. The films were characterized by analysing the chemical composition by Auger Electron Spectroscopy, crystallographic studies by X-ray diffraction and surface morphology by Atomic Force Microscopy. The $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{InSe}_2$ films formed at a substrate temperature of 693 K was found to be nearly stoichiometric, single phase and polycrystalline. The optical absorption studies showed that the fundamental optical band gap

increased from 1.12 eV to 1.15 eV with the increase of substrate temperature from 623 K to 723 K respectively. The optical band gaps of the film formed at a substrate temperature of 693 K were found to be 1.14 eV, 1.19 eV and 1.45 eV respectively for the fundamental, band splitting by crystal-field and spin-orbit effects respectively.

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