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Structural, optical, and electrical properties of flash-evaporated copper indium diselenide thin films

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Abstract Copper indium diselenide ($CuInSe_2$) compound was synthesized by reacting its elemental components, i.e., copper, indium, and selenium, in stoichiometric proportions (i.e., 1:1:2 with 5% excess selenium) in an evacuated quartz ampoule. Structural and compositional characterization of synthesized pulverized material confirms the polycrystalline nature of tetragonal phase and stoichiometry. $CuInSe_2$ thin films were deposited on soda lime glass substrates kept at different temperatures (300–573 K) using flash evaporation technique. The effect of substrate temperature on structural, morphological, optical, and electrical properties of $CuInSe_2$ thin films were investigated using X-ray diffraction analysis (XRD), atomic force microscopy (AFM), optical measurements (transmission and reflection), and Hall effect characterization techniques. XRD analysis revealed that $CuInSe_2$ thin films deposited above 473 K exhibit (112) preferred orientation of grains. Transmission and reflectance measurements analysis suggests that $CuInSe_2$ thin films deposited at different substrate temperatures have high absorption coefficient ($\sim 10^4$ cm^{-1}) and optical energy band gap in the range 0.93–1.02 eV. Results of electrical characterization showed that $CuInSe_2$ thin films deposited at different substrate temperatures have *p*-type conductivity and hole mobility value in the range 19–136 cm^2/Vs. Variation of energy band gap and resistivity of $CuInSe_2$ thin films deposited at 523 K with thickness was also studied. The temperature dependence of electrical conductivity measurements showed that $CuInSe_2$ film deposited at 523 K has an activation energy of $\sim$30 meV.

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Introduction

Copper indium diselenide ($CuInSe_2$) and its quaternary copper indium gallium diselenide (CIGS) are very useful materials for thin film photovoltaic applications. This is clearly demonstrated by the reported high conversion efficiency, i.e., 19.9% for CIGS-based solar cells [1] at laboratory scale. A variety of deposition techniques have been employed by researchers to prepare $CuInSe_2$ thin film for photovoltaic applications. It includes flash evaporation [2–4], sputtering [5], spray pyrolysis [6], electrodeposition [7], screen printing [8], stacked elemental layer deposition [9], etc. Up to now the best results were achieved by evaporation of the elements, either simultaneously or in sequential processes with adjacent treatment. However, for future low cost production simple techniques with high throughput are desirable.

Flash evaporation technique is widely used by researchers to deposit binary/ternary semiconductor compound material owing to its simplicity and ease of operation. In this method, pulverized compound material is transported to an evaporation boat hot enough to provide a quick evaporation of the material. However, poor reproducibility and compositional deviations are the major problems while depositing ternary compound such as

$CuInSe_2$ [10]. We have overcome this problem by keeping the boat temperature high enough ($\sim$1473 K) and reducing the rate of deposition.

Dependences of structural properties on substrate temperature (T_s) of $CuInSe_2$ thin films deposited using flash evaporation technique were reported by Akl et al. [2]. It was observed that films deposited above 473 K substrate temperature were crystalline in nature. Activation energy estimated by Joseph and Menon [4] for $CuInSe_2$ films deposited at different T_s was in the range 0.02–0.48 eV. This paper presents results obtained from a study on the effects of the substrate temperature on the properties of flash-evaporated $CuInSe_2$ films. The structural, compositional, morphological, optical, and electrical properties were investigated using analysis methods including X-ray diffraction (XRD), energy dispersive analysis of X-rays (EDAX), atomic force microscope (AFM), transmittance measurements, and Hall effect techniques.

Experimental details

$CuInSe_2$ compound was synthesized from its constituent elements, i.e., copper (Cu), indium (In), and selenium (Se). Cu, In, and Se weighed in stoichiometric proportion (1:1:2 with 5% excess Se) were sealed in a quartz ampoule at a base pressure of 10^{-2} mbar. The ampoule was placed in an indigenous electrical furnace. The temperature of the furnace was raised from room temperature to 1400 K at the rate of 3 K/min. The ampoule was kept at that temperature for 3 h for uniform mixing and homogeneity of the melt. The ampoule was then cooled down to room temperature at the rate of 4 K/min. The fine-grained starting material was prepared by first grinding and then sieving. $CuInSe_2$ thin films of varying thickness (100–500 nm) were deposited onto organically cleaned glass substrates held at different temperatures ranging from 300 to 573 K using a flash evaporation technique at a base pressure of 10^{-5} mbar. The substrate temperature was measured using chromel–alumel thermocouple kept in good thermal contact with the substrate. The rate of deposition (0.8–1.0 nm/s) and thickness of $CuInSe_2$ films were measured using quartz crystal thickness monitor type (Hind Hi Vac. DTM-101). All the deposition parameters were kept constant except the substrate temperature.

The structural characterization of synthesized compound and $CuInSe_2$ thin films deposited at different substrate temperatures were carried out using an X-ray diffractometer (Rigaku D-Max-III) in 2θ range 10°–70° at a scan rate 0.05 s^{-1} with Cu-K_α radiation source. The chemical composition of the synthesized $CuInSe_2$ powder and thin films deposited at different substrate temperatures was studied using scanning electron microscope (Philips ESEM, 30XL) equipped with EDAX facilities operated at 30 kV with standardless ZAF quantification. AFM (Veeco CP II research head) was employed to probe different portions of the films deposited at different substrate temperatures in non-contact mode. The optical transmittance and reflectance measurements were carried out in the wavelength range 800–1500 nm using the monochromator CM 110, photo detector 818-IR (Newport), and lock-in amplifier SR-530. Standard Hall effect measurements setup having programmable power supply (Keithley 2420-C) and 6½ digit multimeter (Keithley-2000) were used for electrical characterizations of $CuInSe_2$ thin films deposited at different substrate temperatures. Hot probe measurements were also done to verify the conductivity type. The convenient two-probe method was used for electrical conductivity measurements in the temperature range 300–430 K.

Results and discussions

Structural characterization

Figure 1 shows the XRD patterns carried out for $CuInSe_2$ in powder form and thin films of 200 nm thickness grown at four different T_s, viz., 300, 373, 523, and 573 K. The analysis of XRD data shows that synthesized $CuInSe_2$ powder has a polycrystalline nature. XRD peaks at (112), (220), (400), and (312) indicate the presence of chalcopyrite phase. The absence of XRD peaks due to binary alloy or different phases indicates good structural homogeneity

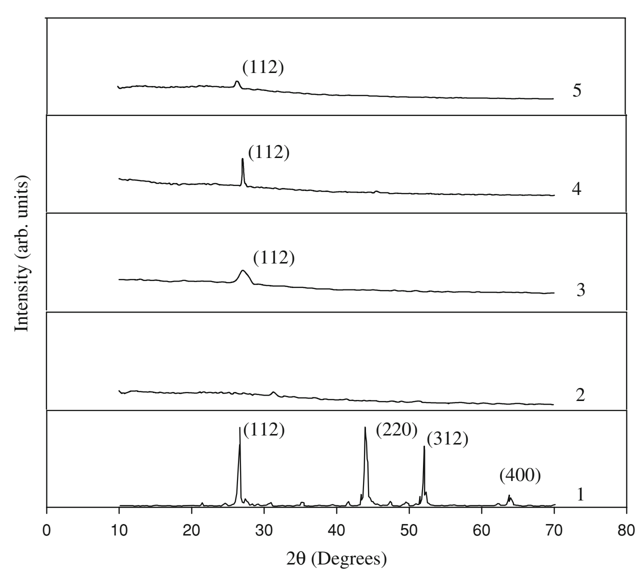

Fig. 1 XRD pattern of $CuInSe_2$ in (1) powder form and thin films deposited at (2) T_s = 300 K, (3) T_s = 373 K, (4) T_s = 523 K, and (5) T_s = 573 K

of synthesized $CuInSe_2$ powder. The (112) preferred orientation and splitting of peaks due to tetragonal structure demonstrate good crystalline quality.

The XRD pattern of $CuInSe_2$ thin film deposited at various substrate temperatures indicate that all the films showed an intense (112) preferred orientation of grains except the film grown at 300 K, which is amorphous in nature. The intensity of (112) peak has been found to increase with increasing T_s up to 523 K while the full-width at half maximum (FWHM) values of $CuInSe_2$ peak decrease showing that the crystalline size increases. For $CuInSe_2$ thin film deposited at 573 K, the intensity of (112) peak and crystallite size decreases. This is due to the change in the stoichiometry of the film.

The mean size of the crystallites in $CuInSe_2$ thin films deposited at different substrate temperatures was calculated from (112) X-ray diffraction peak broadening using the well-known Scherrer's formula [11]:

$$d = \frac{0.9\lambda}{B_r \cos\theta}, \qquad (1)$$

where λ is the wavelength of Cu-K_α radiation ($\lambda = 0.154$ nm), and B_r is the FWHM of (112) peak. The peak position of (112) plane and FWHM of the (112) peak, along with the calculated values of the crystallite size, for films grown at different substrate temperatures are shown in Table 1.

Morphological studies

The surface morphology of $CuInSe_2$ thin films grown at three different substrate temperatures was studied using AFM to observe the microstructure. Figure 2 shows the surface topographical images recorded for $CuInSe_2$ films deposited at different substrate temperatures. AFM image of the film grown at 373 K reveals a structure with dense grains. The root mean square (rms) roughness was 2.14 nm. The surface topography is composed of clusters of varying sizes with irregular shapes. The irregular shape of the grains suggests that at low substrate temperature the kinetic energy is not sufficient for the coalescence of the grains. When the substrate temperature was raised to 523 K, the crystalline structure and clear grain boundaries became apparent. The rms roughness values of the $CuInSe_2$ films grown at 523 and 573 K were 5.75 and 4.84 nm, respectively.

The temperature dependence of growth and morphology can be explained as follows. The evaporated atoms or molecules arriving 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 atoms/molecules. As a result, the collision process initiates the nucleation and

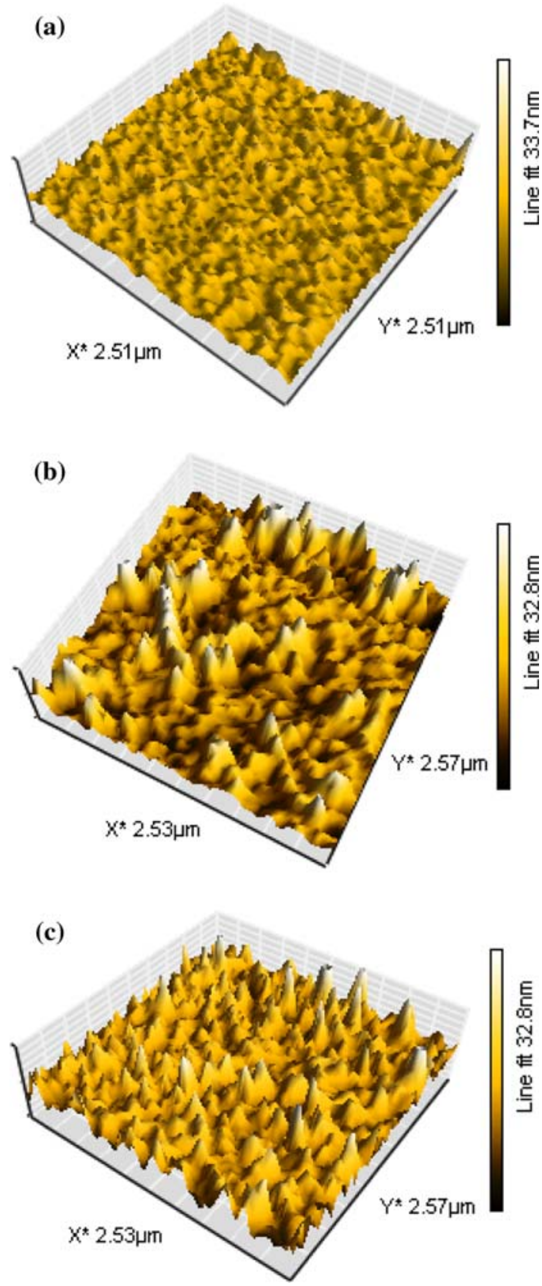

Fig. 2 AFM images (three-dimensional) of the films grown at: **a** $T_s = 373$ K. **b** $T_s = 523$ K. **c** $T_s = 573$ K

Table 1 The position of (112) peak, FWHM, and crystallite size of the films grown at different substrate temperatures

Substrate temperature (T_s) (K)	Position of (112) peak (°)	FWHM (°)	Crystallite size (nm)
373	27.09	0.469	21
523	26.82	0.350	30
573	27.16	0.789	11

enhances the island formation in order to grow continuous films with larger grains.

Compositional characterization

The composition of $CuInSe_2$ is a topic of main importance since many cell properties are influenced by deviations from stoichiometry [12]. The typical EDAX spectrum of synthesized powder is shown in Fig. 3. This analysis shows that the atomic percentage of Cu, In, and Se confirms the stoichiometry of the synthesized compound. The elemental composition determined from EDAX analysis of $CuInSe_2$ thin films deposited at different substrate temperatures is shown in Table 2.

The analysis of data suggests that elemental composition approaches close to stoichiometry (i.e., 1:1:2) with increase in substrate temperature. $CuInSe_2$ thin films deposited at a substrate temperature of 523 K has near-stoichiometric composition of elements.

Optical characterization

The variation of transmittance, T, and reflectance, R, as a function of wavelength for $CuInSe_2$ thin films of ~200 nm thickness deposited at different substrate temperatures is shown in Fig. 4a and b.

It was observed from the transmission spectra that all films have transmittance of 0.2–0.7% in the wavelength range 800–1500 nm depending on the substrate temperature. The peak values of transmission spectra are seen at about 1100–1200 nm, suggesting that the absorption starts about this wavelength. In the near infrared, the transmittance is observed to be less dependent on photon energy above 1200 nm. The decrease of transmittance in the higher photon energy region is due to free carrier absorption.

The transmission and reflection data were analyzed to calculate the refractive index of the films. In the case of normal light incidence, the reflectivity, R, may be expressed in terms of the real refractive index, n, and extinction coefficient, k, by

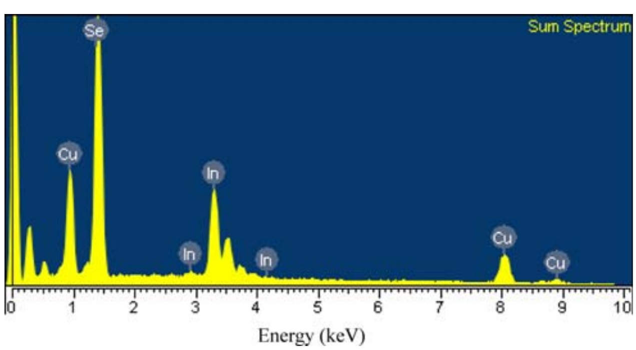

Fig. 3 EDAX diagram of synthesized $CuInSe_2$ powder

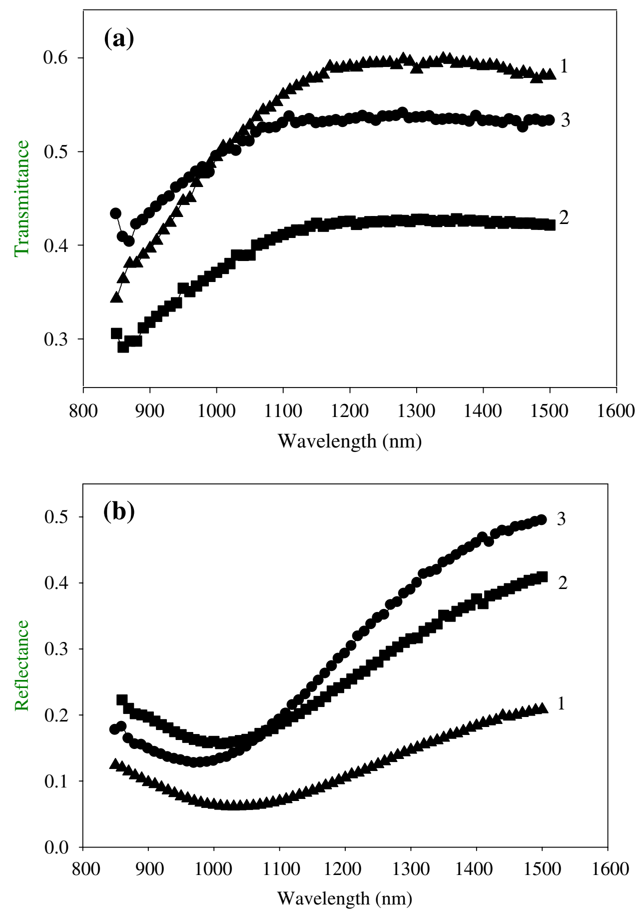

Fig. 4 Spectral variation **a** of transmittance and **b** of reflectance of films deposited at (1) $T_s = 373$ K, (2) $T_s = 523$ K, and (3) $T_s = 573$ K

Table 2 EDAX analysis of synthesized $CuInSe_2$ thin films grown at different substrate temperatures

Substrate temperature (T_s) (K)	Elemental composition (at.%)			Ratio Cu/In	Se/M[a]
	Cu	In	Se		
373	25.96	26.32	47.72	0.98	0.90
523	25.94	24.82	49.24	1.04	0.97
573	22.72	27.70	49.58	0.82	0.98

[a] M = [Cu] + [In]

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}. \quad (2)$$

Solving the above equation for n gives

$$n = \frac{(1+R) + \sqrt{4R - (1-R)^2 k^2}}{1-R}. \quad (3)$$

Figure 5 shows the variation of refractive index of the films with wavelength. It is seen that the film deposited at $T_s = 473$ K has very low value of refractive index in the wavelength range studied while the film deposited at $T_s = 523$ K has refractive index in the range 2.6–2.8, which agrees quite well with the values reported by Dhanam et al. [13].

The absorption coefficient (α) was calculated from the experimentally measured values of reflectance R and transmittance T using the relation [14]

$$\alpha = \frac{1}{t}\left(\ln \frac{(1 - R(\lambda))}{T(\lambda)}\right), \quad (4)$$

where t is the film thickness in nanometer. Figure 6 shows the absorption coefficient α as a function of photon energy for films grown at different substrate temperatures.

The values of absorption coefficient of $CuInSe_2$ thin films deposited at different substrate temperatures were used to calculate the energy band gap. As $CuInSe_2$ is a direct band gap semiconductor, α follows the relation

$$\alpha = \frac{A_0}{h\nu}\sqrt{h\nu - E_0}, \quad (5)$$

where E_0 is the fundamental optical band gap energy and A_0 is an edge width parameter. Figure 7 shows plots of $(\alpha h\nu)^2$ with photon energy $h\nu$ for films grown at different substrate temperatures. Extrapolation of the linear portion of the curve to $(\alpha h\nu)^2 = 0$ gives the band gap energy which is in the range 0.92–1.03 eV. The band gap values of this study are in good agreement with the band gap values obtained in many earlier works [15–17].

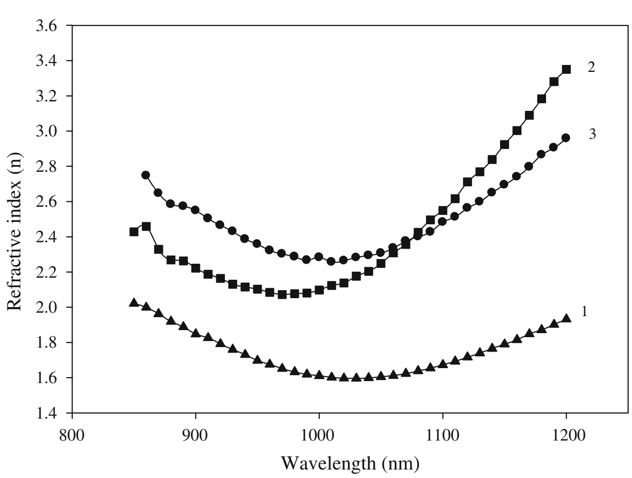

Fig. 5 Refractive index of $CuInSe_2$ films deposited at (1) $T_s = 373$ K, (2) $T_s = 523$ K, and (3) $T_s = 573$ K

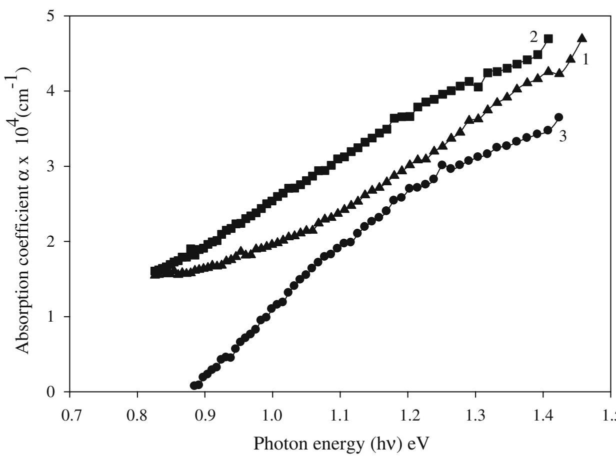

Fig. 6 Absorption coefficient vs. photon energy for films deposited at (1) $T_s = 373$ K, (2) $T_s = 523$ K, and (3) $T_s = 573$ K

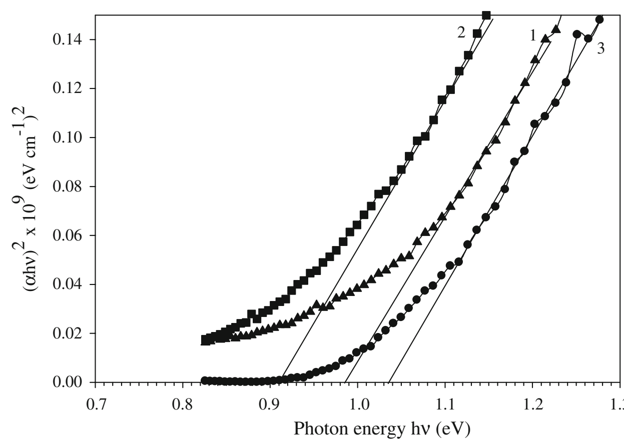

Fig. 7 Plots of $(\alpha h\nu)^2$ vs. $h\nu$ for films deposited at (1) $T_s = 373$ K, (2) $T_s = 523$ K, and (3) $T_s = 573$ K

The variation of optical band gap with thickness for films prepared at 523 K is shown in Fig. 8. The decrease in energy band gap with the thickness may be due to an increase in particle size and decrease in strain and dislocation density.

Electrical characterization

A better understanding of the electrical properties of $CuInSe_2$ thin films are required for the optimization of the preparation conditions to use it as an absorber in solar cell. Hall effect measurements of the as-deposited films of 200 nm thickness were carried out using silver paste as contact material. Figure 9 shows the variation in resistivity and mobility of the films grown at different substrate temperatures. From the graph, it is clear that as the

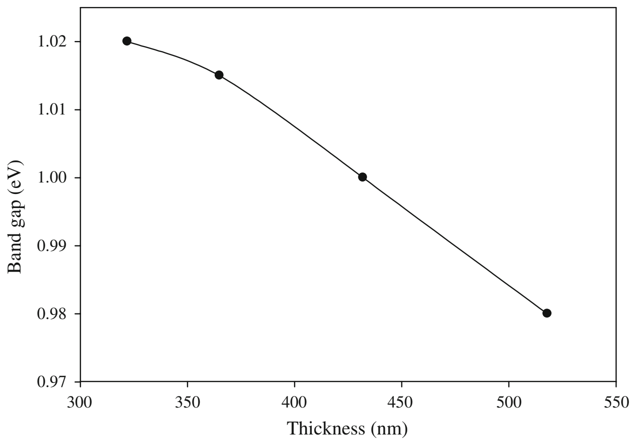

Fig. 8 The variation of optical band gap of $CuInSe_2$ films with thickness

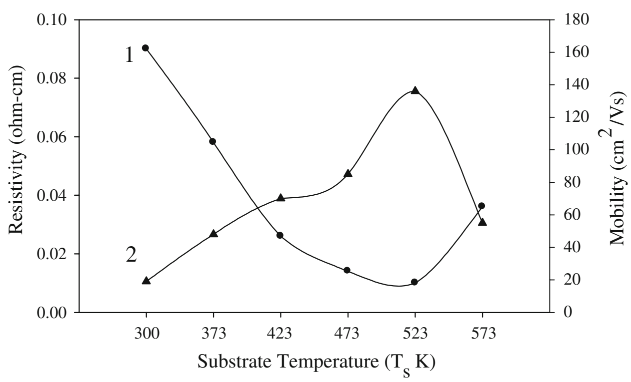

Fig. 9 Variation of resistivity (1) and mobility (2) with substrate temperature

substrate temperature increases mobility increases. This is due to the increase in crystallite size as observed in XRD analysis. The increased crystal size weakens the intercrystalline boundary scattering and increases the carrier lifetime, consequently increasing the mobility.

The decrease in resistivity with the increase in substrate temperature can be explained using Petritz's barrier model [18]. According to this model, at low temperatures the crystallites do not grow sufficiently large, while at higher substrate temperatures large crystallite sizes are obtained which ultimately decrease the intercrystalline barrier. This leads to comparatively narrow intercrystalline barriers, in turn resulting in the decrease of resistivity. The resistivity of the films deposited at a substrate temperature of 573 K increased rapidly, which may be due to the saturation of the grain size. All films had *p*-type conductivity, as identified by the hot probe method, and carrier concentration in the range 10^{17}–10^{18}/cm^3.

$CuInSe_2$ thin film deposited at a substrate temperature of 523 K shows good structural and optical properties as

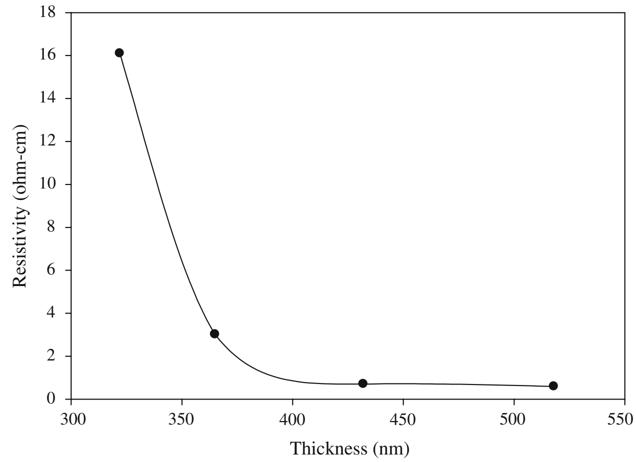

Fig. 10 Resistivity variation with thickness

indicated by XRD, AFM, and transmittance measurements. To observe the changes in the electrical property with thickness, we have deposited films of different thicknesses (from 200 to 500 nm) at a substrate temperature of 523 K. Figure 10 shows the measured electrical resistivity of $CuInSe_2$ films.

The decrease in resistivity with thickness can be interpreted on the basis of grain boundary scattering as discussed by Wu and Chiou [19]. As the thickness increases, the grain size increases; the grain boundary size becomes relatively reduced, which in turn reduces the grain boundary scattering and increases the carrier life time, consequently reducing the resistivity.

Activation energy

In the literature [20], the temperature dependence of semiconductor materials conductivity (σ) is expressed by the relation

$$\sigma = \sigma_0 \exp\left[\frac{-E_a}{kT}\right], \quad (6)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy, and K is the Boltzmann constant. Arrhenius plot of $\ln(\sigma)$ vs. $10^3/T$ of $CuInSe_2$ film deposited at 523 K substrate temperature is shown in Fig. 11. For this, we studied the temperature dependence of resistance of $CuInSe_2$ thin films of $\sim$2000 Å thickness prepared on soda lime glass substrate. The samples were heated without illumination in the temperature range 300–400 K while the resistance was continually measured. The activation energy calculated from linear least square fit of Arrhenius plot is $\sim$30 meV. In the temperature range studied, $CuInSe_2$ thin film exhibited a thermally activated electrical conductivity, and the conduction process is governed by the grain boundaries. Activation energy calculated agrees quite well

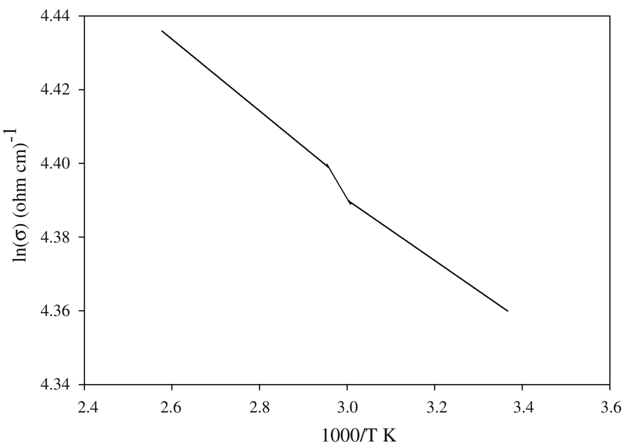

Fig. 11 Arrhenius plot for the film deposited at 523 K

with the reported values [21] for $CuInSe_2$ film prepared using stacked elemental layers.

Conclusions

$CuInSe_2$ compound was synthesized from its constituent elements. Thin films of $CuInSe_2$ were deposited using flash evaporation technique at different substrate temperatures from synthesized stoichiometric compound material. XRD and AFM analyses revealed that the substrate has significant influence on the structural and morphological properties of films. EDAX measurements of films revealed a near-stoichiometric composition of elements. The electrical resistivity obtained from Hall effect measurements was in the range of 10^{-2} Ω cm and was influenced by the substrate temperature. Analysis of optical transmission measurements of $CuInSe_2$ film deposited at different substrate temperatures revealed a value of E_g in the range 0.92–1.03 eV. An absorption coefficient α greater than 10^4 cm^{-1} was observed for all films. The activation energy calculated from temperature-dependent electrical conductivity measurements of $CuInSe_2$ thin film deposited at 523 K is 30 meV.

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