J Mater Sci (2011) 46:6952–6959
DOI 10.1007/s10853-011-5661-y

Influence of substrate and selenization temperatures on the growth of Cu_2SnSe_3 films

G. Hema Chandra · O. Lakshmana Kumar ·
R. Prasada Rao · S. Uthanna

Received: 11 March 2011 / Accepted: 25 May 2011 / Published online: 15 June 2011

Abstract The effects of substrate temperature and selenization temperature on the structure, composition, electrical and optical properties of Cu_2SnSe_3 films were studied systematically. Cu_2SnSe_3 films deposited at various substrate temperatures (303–573 K) by the flash evaporation method are found to be non-stoichiometric. To compensate the selenium deficiency and obtain a single-phase, an annealing Cu_2SnSe_3 films deposited at 573 K was performed in selenium atmosphere. Cu_2SnSe_3 films deposited at a substrate temperature of 573 K and then selenized at 673 K were single phase and polycrystalline exhibiting monoclinic structure. The films showed p-type conductivity with a direct band gap of 0.84 eV.

Introduction

Recently, there has been a great deal of interest on new multinary metal chalcogenide materials [1–3]. These compounds have been used in optoelectronic devices, like lasers and solar cells [4]. I–IV–VI ternary chalcogenides, including Cu–Sn–X (X = S, Se) systems, were traditionally regarded as small or middle band gap semiconductors. These ternary chalcogenide functional materials are suitable for solid lubricant due to their outstanding thermal and mechanical properties.

In I_2–IV–VI_3 family, Cu_2SnS_3 compound semiconductor was found to be a favourable choice for lithium battery electrodes [5], photovoltaics [6], thin film wave guides and light emitting diodes [7]. Cu_2SnSe_3 having low-melting point and mass density and a high-mean atomic weight and refractive index is a good candidate for acousto-optic applications in the IR region [8, 9]. It is also considered as a high-efficiency thermoelectric material [10] and an important precursor material for the growth of promising solar cell absorber layer ($Cu_2ZnSnSe_4$) via solid state reaction of Cu_2SnSe_3 and ZnSe [11].

The highlights of multinary chalcogenide chemistry have been the development of various techniques to prepare structurally and chemically unique compounds. However, the preparation of single crystals of most I_2–IV–VI_3 compound semiconductors is not easy. Very little work has been reported on Cu_2SnSe_3 bulk [12–17] and thin films [18–20]. Cu_2SnSe_3 has exhibited both monoclinic [15–17] and sphalerite structures [18] irrespective of variation in Cu/Sn atomic ratio (1.743–2.03) and Se/(Cu + Sn) atomic ratio (1.075–1.275). Recently, Skoug et al. reported that, the slow cooling of Cu_2SnSe_3 compound resulted in monoclinic structure, whereas, water-quenched compound crystallizes to cubic zincblende-like (sphalerite) structure.

Electronic supplementary material The online version of this article (doi:10.1007/s10853-011-5661-y) contains supplementary material, which is available to authorized users.

G. Hema Chandra · O. Lakshmana Kumar
Materials Science Division, VIT University, Vellore 632 014, Tamil Nadu, India

G. Hema Chandra (✉)
INESC Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal
e-mail: drghc@rediffmail.com

R. Prasada Rao
Department of Materials Science and Engineering, National University of Singapore, Singapore 117 576, Singapore

S. Uthanna
Thin Films Laboratory, Department of Physics, Sri Venkateswara University, Tirupati 517 502, Andhra Pradesh, India

The literature on Cu_2SnSe_3 is minimal [18–20] as far as the thin film form is concerned. A better understanding of the structural, electrical and optical properties is essential for optimizing these films for acousto-optic device applications in the infrared region. Hence, an attempt has been made to study the composition, structure, electrical conductivity and optical absorption studies of Cu_2SnSe_3 thin films prepared by flash evaporation method, followed by selenization. This article reports the growth and characterization of these Cu_2SnSe_3 films.

Experimental details

Ingots of Cu_2SnSe_3 have been prepared using constituent elements (99.999% pure) of copper, tin and selenium (obtained from M/S Aldrich, USA) weighed in stoichiometric ratio. The mixture was sealed in a quartz ampoule under a pressure of less than 1.33×10^{-3} Pa. The sealed ampoule was placed in a vertical furnace, and the temperature was slowly increased at the rate of 30 K h^{-1}, up to 473 K. The ampoule was maintained at that temperature for a period of 24 h to minimize the pressure build up and to avoid possible strong exothermic reactions. The temperature was then increased at the rate of 60 K h^{-1} up to 973 K, beyond which a slow heating process was used to minimize the risk of cracking. The ampoule was kept at 1373 K for a period of 48 h. The quartz ampoule was then cooled slowly to room temperature. The compound was then ground and reduced to 100–300 mesh powder.

Cu_2SnSe_3 thin films were deposited onto ultrasonically cleaned glass substrates by flash evaporation technique in vacuum (5.33×10^{-4} Pa) in the temperature range 303–573 K using a 12A4D Hind Hivac coating unit. The powder was gradually dropped onto a molybdenum boat heated to 1773 K through a controllable vibratory spiral feeder resulting in the flash evaporation of the material. The evaporation rate was about 2 nms^{-1}. The thickness of the films was 300 nm and was monitored using a quartz crystal thickness monitor (QM 101) during deposition. The deposited films were uniform, pinhole free, and strongly adherent to the substrate. Since the Cu_2SnSe_3 films deposited at various substrate temperatures (303–573 K) by flash evaporation method showed non-stoichiometry, an attempt has been made on selenization of these thin film samples deposited at $T_S = 573$ K. The selenization process was conducted for Cu_2SnSe_3 thin films, grown at $T_S = 573$ K, in a partially closed graphite box containing pure selenium powder. The box was then introduced into a quartz tube of horizontal furnace evacuated to 1.33×10^{-1} Pa by rotary pump in an argon atmosphere. The graphite box reduces the re-evaporation of selenium during annealing. The selenization process was realized in a two-step heating. In the first step, the temperature was slowly increased up to 423 K and maintained there for 30 min to saturate the alloy with selenium. Later in the second step, the temperature was increased slowly up to 623 or 673 K and maintained there for 60 min to re-crystallize the pre-reacted sample. The thickness of the selenized samples was measured with a Dektak IIA surface profiler with an error of ±5 nm. The elemental composition of the ingot and films was determined using energy dispersive X-ray analysis (EDX) attached to a JEOL scanning electron microscope (SEM). The accelerating voltage used to generate the high-energy electrons was 20 kV. JEOL EDX system internal standards were considered for the measurements with an error of ±1 at.%. The optical transmittance and reflectance of the films were recorded at room temperature in the wavelength range 500–2500 nm using UV–vis–NIR double beam spectrophotometer. X-ray diffraction patterns of ingot and the films were recorded with Philips X-ray diffractometer using Cu K_α radiation ($\lambda = 0.15406$ nm). The patterns were recorded with a scan speed of $0.02° s^{-1}$ in the 2θ range 10°–80°. The TOPAS 2.0 X-ray analytical tool (software) from Bruker AXS 2000 was used to establish the position of peaks. The structural refinement was carried out using Rietveld method. The temperature dependence of electrical conductivity was measured by the standard van der Pauw method in the range 303–483 K.

Results and discussion

Characterization of Cu_2SnSe_3 compound

Scanning electron microscope image of the powder crystals, an energy dispersive X-ray spectra and an X-ray diffraction pattern of the prepared Cu_2SnSe_3 compound are shown in the Fig. 1a–c, respectively. The powder looks like sharp edged gravel with different sizes and dimensions (100–400 μm). Different parts of the Cu_2SnSe_3 ingot were examined by the EDX analysis, as shown in Fig. 1b. It was observed from the analysis that the ingot was nearly stoichiometric and homogenous in nature (Cu: 35.1, Sn: 17.3 and Se: 47.6 in at.%). The Cu/Sn ratio of the prepared compound is 2.03 (slightly copper rich) and Se/(Cu + Sn) is 0.91 (deficiency of selenium over cations). The prepared compound was then characterized by the X-ray diffractometer. The XRD pattern of bulk Cu_2SnSe_3 is shown in Fig. 1c. Rietveld refinement (shown in supplementary data) indicates the formation of Cu_2SnSe_3 compound having the sphalerite structure with a space group of $F\bar{4}3m$ with unit cell parameter $a = 0.569$ nm, which matches with the standard values [3, 14, 21]. The diffraction pattern also contained weak additional peak indicating the presence of a secondary phase in the synthesized material. This peak was identified as belonging to orthorhombic phase of Cu_3Sn (ICDD card no. 65-4653). The formation of the secondary phase (Cu_3Sn) might be due to slight deviation in the stoichiometry, as verified from EDX analysis of Cu_2SnSe_3 compound.

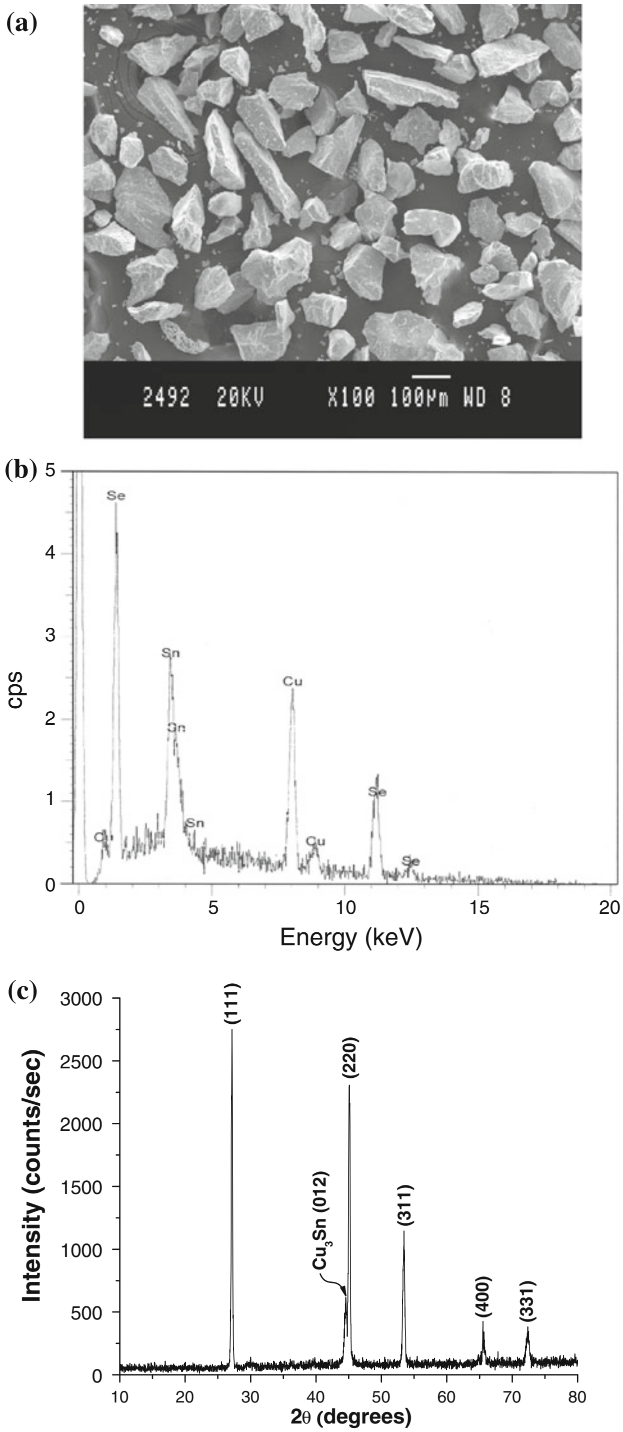

Fig. 1 **a** SEM image of Cu_2SnSe_3 powder crystals, **b** energy dispersive X-ray analysis spectra of Cu_2SnSe_3 compound and **c** X-ray diffraction spectra of Cu_2SnSe_3 compound

Characterization of Cu_2SnSe_3 films

The energy dispersive X-ray spectra of Cu_2SnSe_3 thin films revealed that the Cu, Sn and Se contents depend critically on the deposition temperature (T_S). Figure 2a shows the variation of elemental atomic percentage of Cu, Sn and Se with T_S for Cu_2SnSe_3 films of 300 nm thickness. It is seen that Cu_2SnSe_3 thin films formed at $T_S < 523$ K contained excess tin and selenium, and were deficient in copper. This might be due to the difference in the vapour pressures of the elements [22] in the Cu_2SnSe_3 compound ($P_{Se} > P_{Sn} > P_{Cu}$). The films deposited at $T_S = 573$ K contain excess copper and tin, and were deficient in selenium. The decrease of at.% of selenium for the films grown at $T_S = 573$ K indicates loss of selenium due to re-evaporation from the surface of the sample. Since Cu_2SnSe_3 films deposited at various temperatures (303–573 K) by the flash evaporation method are found to be non-stoichiometric, an attempt was made on annealing of Cu_2SnSe_3 thin films deposited at $T_S = 573$ K in vacuum at 623 and 673 K in selenium environment. Figure 2b shows the energy dispersive X-ray analysis spectra of Cu_2SnSe_3 films (324 nm) deposited at 573 K and selenized at $T_A = 673$ K. The films deposited at $T_S = 573$ K and selenized at $T_A = 673$ K were nearly stoichiometric, and the calculated atomic percentages (at.%) of copper, tin and selenium are 31.7, 16.1 and 52.2, respectively, which are comparable to the stoichiometric material composition (at.%: Cu = 33.3, Sn = 16.6 and Se = 50.1). The variation in elemental atomic percentages of Cu, Sn and Se with substrate and selenization temperatures for Cu_2SnSe_3 films are shown in Table 1.

The X-ray diffraction (XRD) studies of as deposited Cu_2SnSe_3 films grown at different substrate temperatures (T_S) demonstrated the presence of SnSe phase in the films and an improvement in the crystallinity with an increase in substrate temperature. Cu_2SnSe_3 films grown at substrate temperatures of 303–373 K showed amorphous nature. Figure 3 depicts the XRD pattern of Cu_2SnSe_3 films grown at four typical substrate temperatures of 423, 473, 523 and 573 K, respectively. The films grown at substrate temperatures from 473 to 573 K exhibited two phases, namely Cu_2SnSe_3 and SnSe. The peaks observed at $2\theta = 30.47°$, 31.13°, 37.80° and 49.72° are due to the SnSe phase corresponding to (111), (400), (311) and (511) which closely matches with the ICDD card no. 48-1224.

Figure 4 shows the XRD pattern of the Cu_2SnSe_3 films formed at $T_S = 573$ K and selenized (T_A) at 623 and 673 K, respectively. The films deposited at a substrate temperature of 573 K and then selenized (T_A) at 623 K showed SnSe phase along with Cu_2SnSe_3. The peaks

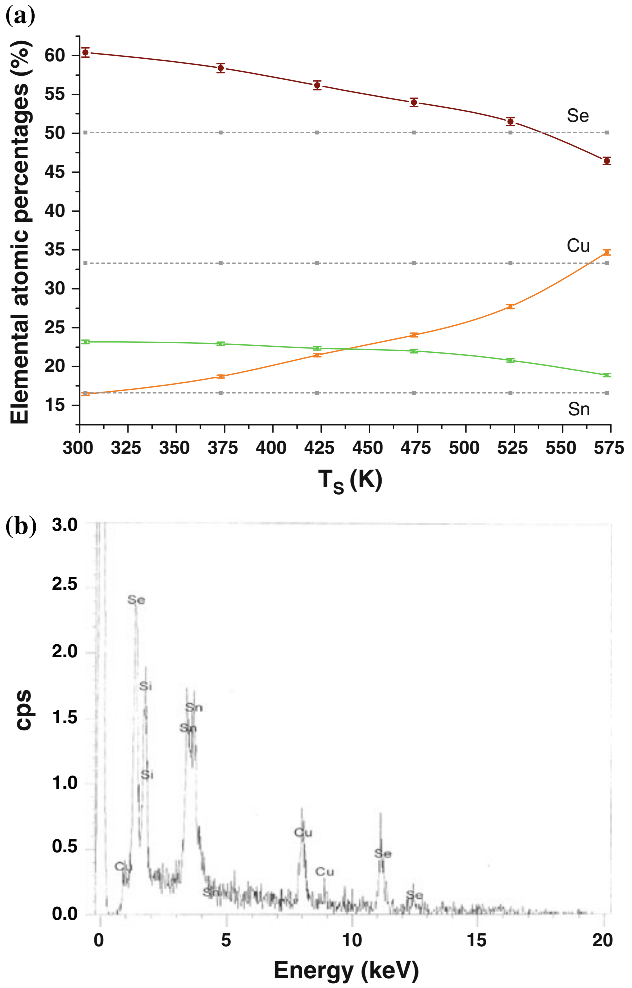

Fig. 2 **a** Elemental atomic percentages of Cu, Sn, Se with T_S for Cu_2SnSe_3 thin films (300 nm). **b** Energy dispersive X-ray analysis for Cu_2SnSe_3 thin film (324 nm) grown at 573 K and selenized at 673 K

Table 1 Composition of constituent elements in Cu_2SnSe_3 films by varying substrate and selenization temperatures

T_S (K)	Cu	Sn	Se
303	16.4	23.2	60.4
373	18.7	22.9	58.4
423	21.4	22.4	56.2
473	24.0	22.0	54.0
523	27.7	20.8	51.5
573	34.7	18.9	46.4
$T_S = 573$ Kand $T_A = 623$ K	27.1	19.5	53.4
$T_S = 573$ K and $T_A = 673$ K	31.7	16.1	52.2

observed at $2\theta = 25.32°$, $29.43°$, $30.47°$, $31.14°$, $37.80°$ and $43.34°$ are due to the SnSe phase corresponding to (201), (011), (111), (400), (311) and (411), which matches with the ICDD card no. 48-1224. The SnSe phase was found to be completely suppressed for the films deposited at $T_S = 573$ K and then selenized at 673 K. The films deposited at $T_S = 573$ K and then selenized at $T_A = 673$ K were single phase, nearly stoichiometric, polycrystalline and exhibited monoclinic structure with a strong (200) preferred orientation.

The peaks at $2\theta = 27.07°$, $31.01°$, $45.06°$ and $53.34°$ are due to the Cu_2SnSe_3 phase corresponding to (200), (022), (−331) and (331) orientations, respectively, which are in good agreement with the reported date of Cu_2SnSe_3 compound by Delgado et al. [17]. The intensity of Cu_2SnSe_3 phase oriented along (200) plane increased with the increase of the substrate temperature and selenization temperatures. A maximum intensity was observed in the XRD pattern for the films deposited at $T_S = 573$ K and then selenized at $T_A = 673$ K. The Rietveld refinement for these films was carried out using the Cu_2SnSe_3 data reported by Delgado et al. [17] as a starting point. The lattice parameters evaluated from Rietveld refinement (shown in supplementary data) for nearly stoichiometric, polycrystalline Cu_2SnSe_3 thin films deposited at 573 K and then selenized at 673 K were found to be $a = 0.694$ nm, $b = 1.213$ nm, $c = 0.694$ nm and $\beta = 109.19°$. This is in good agreement with reported values of Cu_2SnSe_3 semiconducting compound prepared by vertical Bridgman–Stockbarger technique [17].

Figure 4b shows the 3D projection of the compound Cu_2SnSe_3 generated with the atomic coordinates and relevant geometrical parameters obtained from Rietveld analysis data [23] and using Material Studio 4.4 visualizer (Accelrys) program [24]. The structure reveals the possible coordination among Cu, Sn and Se atoms. Each anion (Cu or Sn) is coordinated with four cations (Se) located at the corners of a slightly distorted tetrahedron. The bond distances of Cu–Se and Sn–Se are 0.2436 and 0.2596 nm, respectively, which are in good agreement with reported values [17]. The bond angles of Se–Cu–Se and Se–Sn–Se are 111.75° and 107.77°, respectively, they are slightly low for Se–Cu–Se (115.1°) and high for Se–Sn–Se (105.1°) in comparison with reported values [17], but are close to the ideal tetrahedral bond angle.

The SEM micrographs of Cu_2SnSe_3 films formed at different substrate temperatures and selenization temperatures are shown in Fig. 5. The films formed at 473 K showed a large number of particles uniformly distributed throughout the surface. Crystallites have a coarse-grained shape with mean grain size of around 90 nm. As the deposition temperature increased to 573 K, the grain size of the films increases due to surface migration of the adsorbed atoms, resulting in enhanced interactions between the adsorbed atoms to form larger grains. As-grown flash-evaporated films reveal that the deposition temperature has a significant

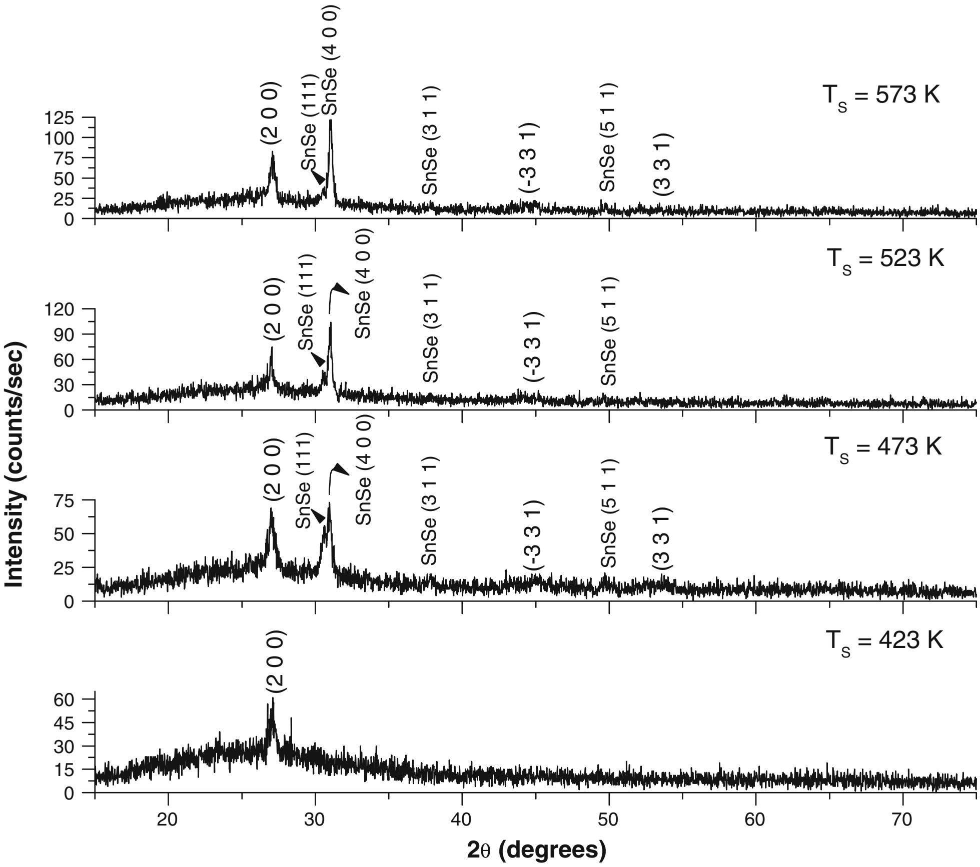

Fig. 3 X-ray diffraction pattern of Cu_2SnSe_3 thin films (300 nm) deposited at four typical substrate temperatures 423, 473, 523 and 573 K, respectively

effect on grain growth and it follows known nucleation and film formation processes. The films formed at 573 K showed an enhancement in the particle size with different well-defined shapes (spherical, triangular, rectangular, etc.) with mean grain size of around 120 nm. Further improvement in the grain size was observed for the films deposited at $T_S = 573$ K and selenized at $T_A = 673$ K. The surface shows an agglomeration of the grains grown perpendicular to the surface for films deposited at $T_S = 573$ K and selenized at 673 K. The enhancement in the grain size was confirmed from the XRD pattern of Cu_2SnSe_3 films deposited with increase in substrate and selenization temperatures.

The variation of the electrical resistivity of Cu_2SnSe_3 thin films, of 300 nm thickness, with the substrate temperature is shown in Fig. 6a. The change in the electrical resistivity of the films grown at different substrate temperatures and subjected to various selenization temperatures is due to uncontrolled nucleation and growth of crystallites due to the non-uniformity in the stoichiometry of the films. The electrical resistivity varied from 124 to 16 Ω cm with an increase in substrate temperature from 303 to 573 K. The electrical resistivity values for the films deposited at $T_S = 573$ K and selenized at 623 and 673 K are 2.66×10^{-1} and 6.34×10^{-2} Ω cm, respectively. The decrease in electrical resistivity of the as-deposited films with increasing T_S from 303 to 573 K and selenization temperature 623–673 K can be explained using the Petritz barrier model [25]. Since the crystallites do not grow sufficiently large at low temperatures, the intercrystalline regions are offering a high resistance to the movement of the charge carriers. At high substrate and selenization temperatures, the formation of fewer nucleation centres results in large crystallite sizes, which ultimately decrease the intercrystalline barriers, and this may be responsible for the decrease in the electrical resistivity. The films deposited at $T_S =$ 573 K and selenized at 673 K were found to be p-type conductive, as verified by the hot probe method. The variation of electrical conductivity with inverse temperature of polycrystalline Cu_2SnSe_3 thin films formed at $T_S = 573$ K and selenized at $T_A = 673$ K is shown in Fig. 6b. The measured d.c. conductivity could fit into the relation

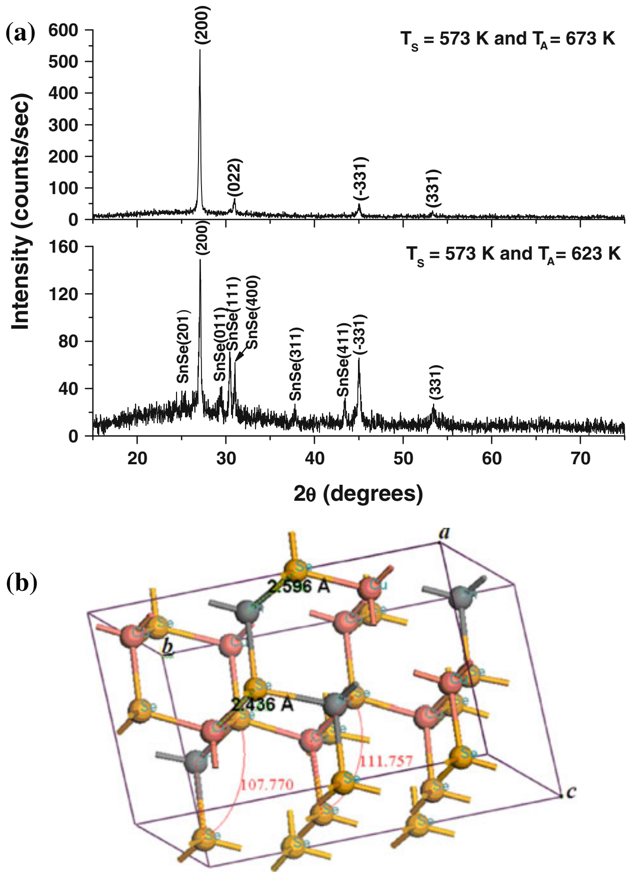

Fig. 4 **a** X-ray diffraction pattern of Cu_2SnSe_3 thin films deposited at 573 K and selenized at 623 and 673 K. **b** The unit cell diagram for Cu_2SnSe_3, showing the possible fourfold coordination of $CuSe_4$ and $SnSe_4$

$$\sigma = \sigma_o^- \exp\left(\frac{-\Delta E}{KT}\right), \tag{1}$$

where σ_o^- and ΔE represent the pre-exponential factor and the activation energy, respectively. The evaluated activation energy was found to be 0.074 eV in the temperature range 303–483 K. The observed activation energy is attributed to a possible negative defect level arising out of slight deviation in stoichiometry. The compositional analysis revealed that the samples deposited at 573 K and selenized at 673 K were slightly Cu-poor and Se-rich. Hence, the possible defect levels are selenium interstitials, copper vacancies and tin on copper sites. The acceptor state with activation energy 74 meV is attributed to a defect level of selenium. This is in reasonable agreement with reported value of 70 meV in single crystals [9, 26].

The optical transmittance and reflectance spectra of the Cu_2SnSe_3 film deposited at $T_S = 573$ K and selenized at $T_A = 673$ K are shown in the Fig. 7a. The optical absorption coefficient (α) was calculated from the optical transmittance (T) and reflectance (R) data by employing the relation

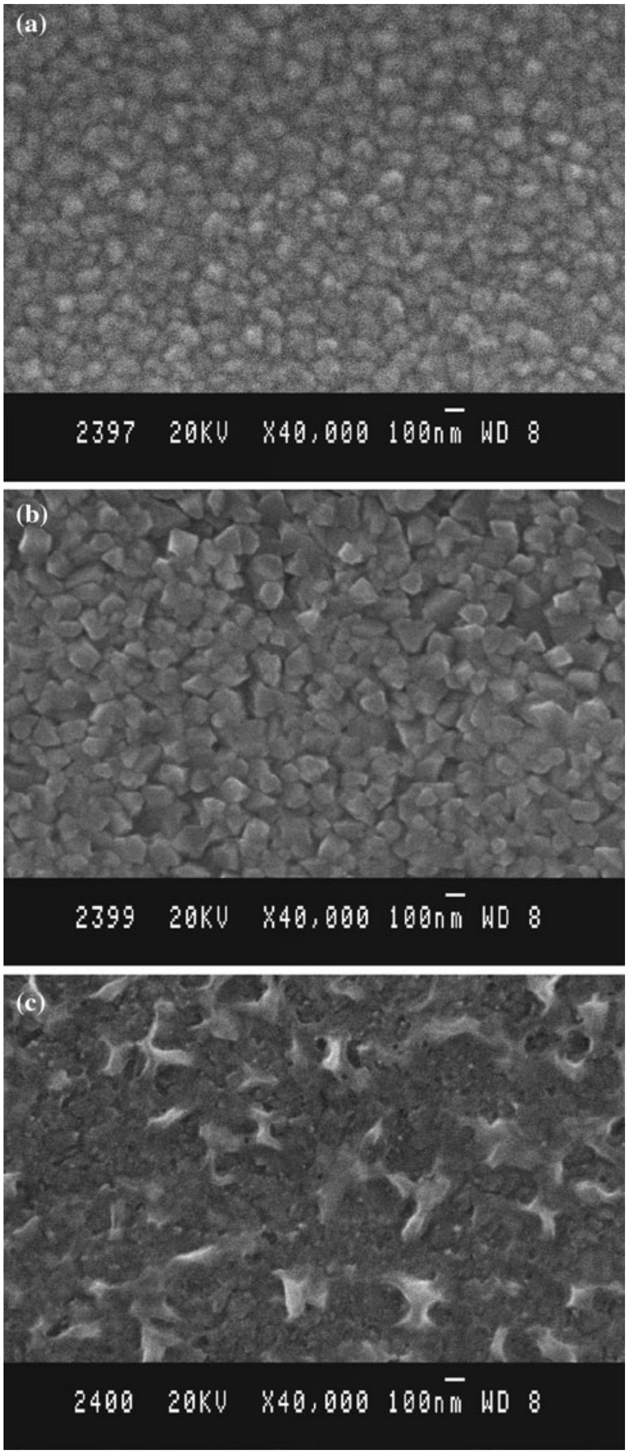

Fig. 5 SEM image of Cu_2SnSe_3 thin films. **a** Deposited at 473 K. **b** Deposited at 573 K. **c** Deposited at 573 K and selenized at 673 K

$$\alpha = \left(\frac{1}{t}\right) \ln\left[\frac{T}{(1 - R)^2}\right], \tag{2}$$

where t is the thickness of the film.

Assuming a direct transition between the top of the valence band and the bottom of the conduction band, the optical band gap (E_g) of the films can be estimated using the relation [27]

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \tag{3}$$

where A is the edge width parameter and $h\nu$ is the photon energy. Figure 7b shows the plot of $(\alpha h\nu)^2$ versus $h\nu$ for the films grown at $T_S = 573$ K and selenized at $T_A = 673$ K. The optical band gap of the film was determined from the extrapolation of the linear plot of $(\alpha h\nu)^2$ versus $h\nu$ at $\alpha = 0$, and it was found to be a direct allowed band gap of 0.84 eV (within the experimental uncertainty of ±0.02 eV). This value is in good agreement with the reported value for Cu_2SnSe_3 crystal [9] and also, Cu_2SnSe_3 films sputtered using a target (Cu_2Se and $SnSe_2$ in 1.8:1 molar ratio) at 673 K, followed by annealing at 773 and 823 K in $SnSe_2$ or Se environment [20].

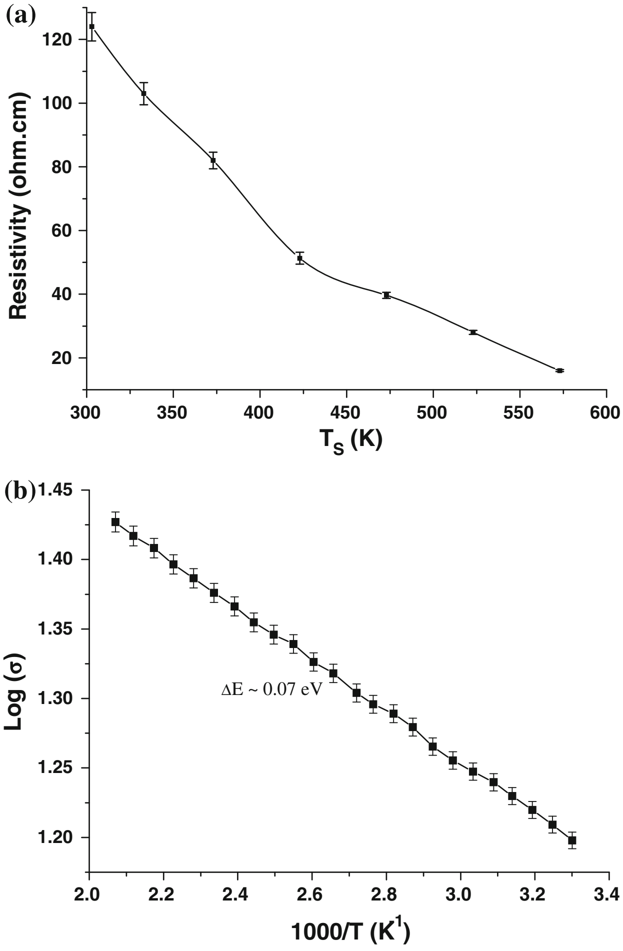

Fig. 6 **a** Variation of electrical resistivity of Cu_2SnSe_3 thin films (300 nm) deposited at different substrate temperatures. **b** Plot of log (σ) as function of $1/T$ for Cu_2SnSe_3 thin films (324 nm) deposited at 573 K and selenized at 673 K

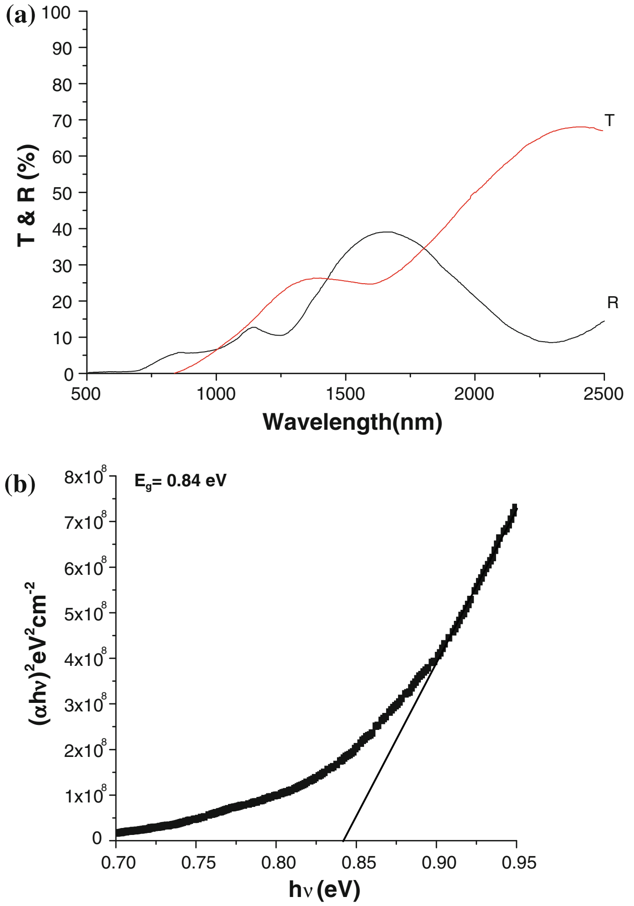

Fig. 7 **a** Optical transmittance and reflectance spectra of Cu_2SnSe_3 films (324 nm) deposited at 573 K and selenized at 673 K. **b** Plot of $(\alpha h\nu)^2$ against $h\nu$ of Cu_2SnSe_3 thin films (324 nm) deposited at 573 K and selenized at 673 K

Conclusion

Cu_2SnSe_3 thin films were prepared by the flash evaporation technique onto glass substrates kept at temperatures in the range 303–573 K, at 5.33×10^{-4} Pa, using a Hind Hivac coating unit. Cu_2SnSe_3 thin film samples deposited at $T_S = 573$ K were annealed at various temperatures in selenium environment. The films grown at 573 K and selenized at 673 K were nearly stoichiometric, single phase, polycrystalline and exhibited monoclinic structure. These Cu_2SnSe_3 thin films (324 nm) showed an electrical resistivity of 6.34×10^{-2} Ω cm, with p-type conductivity. The temperature dependence of electrical conductivity indicated that the activation energy was 0.074 eV in the temperature range 303–483 K. The optical absorption studies indicated a direct band gap of 0.84 eV with high-absorption coefficient (>10^4 cm^{-1}) near the fundamental edge.

Acknowledgements The authors are thankful to the Defence Research and Development Organization, New Delhi, India, for providing financial support to carry out the present research work.

References

1. Disalvo FJ (1991) Science 247:649
2. Sheldrick WS, Wachhold M (1997) Angew Chem Int Ed Engl 36:206
3. Berger LI, Prochukhan VD (1969) Ternary diamond like semiconductors. Consultants Bureau, New York
4. Samanta LK, Ghosh DK, Bhar GC (1986) Phys Status Solidi A 93:k5
5. Wu C, Hu Z, Wang C, Sheng H, Yang J, Xie Y (2007) Appl Phys Lett 91(14):143104
6. Kuku TA, Fakolujo OA (1987) Sol Energy Mater 16:199
7. Marcano G, Rincón C, Marin G, Tovar R, Delgado G (2002) J Appl Phys 92:1811
8. Marcano G, Bracho DB, Rincón C, Sánchez Pérez G, Nieves L (2000) J Appl Phys 88:822
9. Marcano G, Rincón C, de Chalbaud LM, Bracho DB, Sánchez Pérez G (2001) J Appl Phys 90:1847
10. Skoug EJ, Cain JD, Morelli DT (2010) J Alloys Compd 506:18
11. AdhiWibowo R, Jung WH, Al-Faruqi MH, Amal I, Kim KH (2010) Mater Chem Phys 124:1006
12. Palatnik LS, Koshkin VM, Galchinetskii LP, Kolesnikov VI, Komnik YF (1962) Sov Phys Solid State 4:1052
13. Sharma BB, Ayyar R, Shing H (1977) Phys Status Solidi A 40:691
14. Rivet J, Flahaut J, Laruelle P (1963) Compt Rend 257:161
15. Marcano G, de Chalbaud LM, Rincón C, Sánchez Pérez G (2002) Mater Lett 53:151
16. Marcano G, Rincón C, López SA, Sánchez Pérez G, Herrera-Pérez JL, Mendoza-Alvarez JG, Rodríguez P (2011) Solid State Commun 151:84
17. Delgado GE, Mora AJ, Marcano G, Rincón C (2003) Mater Res Bull 38:1949
18. Suresh Babu G, Kishore Kumar YB, Bharath Kumar Reddy Y, Sundara Raja V (2006) Mater Chem Phys 96:442
19. Kuo D-H, Haung W-D, Huang Y-S, Wu J-D, Lin Y-J (2010) Thin Solid Films 518:7218
20. Kuo D-H, Haung W-D, Huang Y-S, Wu J-D, Lin Y-J (2010) Surf Coat Technol 205:S196
21. Palatnik LS, Koshkin VM, Galchinetskii LP, Kolesnikov VI, Komnik YF (1962) Fiz Tverd Tela 4:1430
22. Roth A (1980) Vacuum technology, 2nd edn. North-Holland, Amsterdam
23. Rietveld HM (1969) J Appl Cryst 2:65
24. Materials Studio (2007) Version 4.2. Accelrys Inc., San Diego, CA
25. Petritz RL (1956) Phys Rev 104:1508
26. Goryunova NA, Averkieva GK, Vaipolin AA (1965) Physics: proceedings of 23rd Science conference at Leningrad structural Engineering Institute (in Russian), Leningrad, p 52
27. Tauc J (1974) Amorphous and liquid semiconductors. Plenum Press, New York, NY