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Deposition and Characterization of SnSe and CuInSe₂ Thin Films by Thermal Evaporation Technique from Synthesized SnSe and CuInSe₂ Sources

(Pengenapan dan Pencirian Filem Nipis SnSe dan CuInSe₂ dengan Kaedah Penyejatan Haba Menggunakan SnSe dan CuInSe₂ Sebagai Bahan Sumber)

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ABSTRACT

Tin selenide (SnSe) and copper indium diselenide (CuInSe₂) compounds were synthesized by high temperature reaction method using combination of sealed ampoule (at relatively low pressure $\sim 10^{-1}$ Pa without inert gas) and heating at specific temperature profile in rocking furnace. Powder X-Ray diffraction analysis showed that the products involved only single phases of SnSe and of CuInSe₂ only. Using the reaction products as source materials, the SnSe and CuInSe₂ thin films were vacuum-deposited on glass substrates at room temperature. Structural, elemental, surface morphological and optical properties of the as-deposited films were studied by X-Ray diffraction (XRD), energy dispersive X-Ray (EDX) analysis, field emission scanning electron microscopy (FESEM) and UV-Vis-NIR spectroscopy. Single phase of SnSe and CuInSe₂ films were obtained by thermal evaporation technique from synthesized SnSe and CuInSe₂ compound without further treatment.

Keywords: CuInSe₂; SnSe; solid state reaction; source material; thin films

ABSTRAK

Sebatian timah selenida (SnSe) dan kuprum indium diselenida (CuInSe₂) telah disintesis pada tindak balas bersuhu tinggi menggunakan gabungan ampul yang ditutup kedap (pada kadar tekanan rendah $\sim 10^{-1}$ Pa tanpa gas lengai) dan pemanasan pada profil suhu khusus dalam relau berayun. Analisis pembelauan sinar-X serbuk mendapati hasil sintesis yang diperolehi adalah SnSe dan CuInSe₂ fasa tunggal. Serbuk yang telah disintesis digunakan sebagai bahan sumber untuk menyediakan filem nipis SnSe dan CuInSe₂ menggunakan kaedah penyejatan dengan haba di dalam vakum. Kajian sifat struktur, komposisi, morfologi dan optik untuk filem yang diaplikasikan dijalankan dengan menggunakan pembelauan sinar-X (XRD), analisis penyerakan tenaga sinar-X (EDX), mikroskopi medan pancaran pengimbasan elektron (FESEM) dan spektroskopi UV-Vis-NIR. SnSe dan CuInSe₂ fasa tunggal dapat diperolehi tanpa melalui rawatan selanjutnya melalui kaedah penyejatan dengan haba di dalam vakum menggunakan sebatian SnSe dan CuInSe₂ yang telah disintesis sebagai bahan sumber.

Kata kunci: Bahan sumber; CuInSe₂; filem nipis; SnSe; tindak balas keadaan pepejal

INTRODUCTION

Considerable attention has been paid to prepare metal chalcogenide thin films by different techniques such as chemical bath deposition, chemical vapor deposition, electrodeposition and vacuum evaporation methods (Fujii et al. 1988; John et al. 1994; Pandey et al. 2000; Amaraj et al. 2004; Hilal et al. 2009; Chate et al. 2010; Indirajith et al. 2010; Yunos et al. 2011). Among those, vacuum evaporation is the favorable method to prepare semiconductor thin films for photovoltaic solar cells (Fujii et al. 1988; Tomakin et al. 2011). This is a simple technique that involves easy to control processing parameters, without participation of other atoms or molecules and offers extremely clean interfaces during processing and subsequent consolidation by conducting the experiments under ultra high vacuum conditions (Hass et al. 1993).

However, the source material is crucial in vacuum evaporation technique. Thin film properties depend on the quality of the source material and preparation methodology. Researchers prepare binary, ternary or quaternary compounds in powder form using wet and solid state chemical reactions by introducing and/or replacing a third and fourth element into a metal selenide to tailor the band gap (Chakrabarti et al. 1996). The resulting material is then used as source material in vacuum evaporation. Zulkarnain et al. (2003) and Indirajith et al. (2010) prepared SnSe powders by chemical techniques where the obtained SnSe needed further processing, such as washing and annealing to obtain pure SnSe and to remove secondary phases and unreacted excess elemental substances, such as selenium from the desired compound. The single phase SnSe powder is then used as a source material for vacuum evaporation. Yunos et al. (2011) prepared CuSnSe films

by evaporation technique using direct mixed powder of copper, tin and selenium in stoichiometric ratio (2:1:3) as source. The resulting as-deposited and annealed thin films involved two phases of Cu_2SnSe_3 and SnSe . Yamaguchi et al. (2009) synthesized the copper zinc tin sulfide (CZTS) from its constituent elements by heat treatment followed by a two-stage sulfurization process. Kheraj et al. (2013) used the excess sulfur to facilitate the formation of stoichiometric CZTS phase without going through an extra stage of sulfurization.

Muller et al. (2006) prepared the CuInSe_2 thin films by radio frequency sputtering in argon atmosphere using a CuInSe_2 ceramic target. A nearly stoichiometric film was obtained at substrate temperature below 200°C . Hasan et al. (2000) prepared CuInSe_2 thin film on glass substrates using high vacuum evaporation technique in stacked layers in sequence of elemental indium, selenium and copper. However, stoichiometric films needed further annealing treatment at 350°C .

Vacuum evaporation method has successfully been used for depositing metal chalcogenides of binary, ternary or quaternary compounds. A number of techniques were used to evaporate the synthesized source materials in the vacuum evaporation systems. Thermal evaporation, laser ablation, sputtering, electrical arc discharge and plasma heating have all been reported by Koch (2007). Particle size, uniformity and homogeneity of the source material affect the resulting film properties distinctively when synthesizing selenide-based thin film semiconductor electrodes (Fujii et al. 1988; Kim et al. 2009; Zainal et al. 2003). SnSe and CuInSe_2 thin films are becoming increasingly important in modern applications, such as solar cells and photodetectors, due to their high absorption coefficients and direct band gaps (Fearheiley 1986; Hasan et al. 2000; Indirajith et al. 2010; Zainal et al. 2003). This paper describes a simple technique to prepare source materials for SnSe and CuInSe_2 thin films. An easier ampoule sealing technique and modified rocking tube furnace is to provide proper mixing during melting to increase sample homogeneity. The system was thus designed to maintain homogenous mixing of constituent elements in the desired stoichiometric ratio while avoiding contamination. Then SnSe and CuInSe_2 thin films were prepared by the thermal vacuum deposition, each from

its corresponding source material, which was originally produced by the simple technique. All source materials and films were characterized with crystallinity, composition, surface morphology, and optical properties.

EXPERIMENTAL DETAILS

The polycrystalline SnSe compound was synthesized from its constituent elements, Sn and Se, which were weighed in stoichiometric ratio (1:1) and sealed in a quartz ampoule at base pressure of 0.33 Pa. The polycrystalline CuInSe_2 compound was also synthesized from its constituent elements, Cu, In and Se, which were weighed in stoichiometric ratio (1:1:2) and sealed in a quartz ampoule at same base pressure used for SnSe . The elements, Sn, Cu and Se were purchased from Alfa Aesar with nominal purity 99.8%, 99.5% and 99.5%, respectively. Indium was purchased from Sigma Aldrich with a nominal purity 99.99%. The ampoules were heated using a rocking furnace. In preparing SnSe compound, the furnace temperature was raised to 230°C from room temperature and kept for 2 h to allow selenium to diffuse into tin. The temperature was then raised to 250°C and kept for 2 h to allow both individual components to completely melt and then raised to 1000°C . Furnace temperature ramp rate was set at $5^\circ\text{C}/\text{min}$. To ensure proper mixing and sample homogeneity, the furnace was kept for 2 h and then rocked at a frequency 3 cycle/min with an angle 45° for 48 h. After the desired time, the heated ampoule was then quenched rapidly in liquid nitrogen to get the required compound (Devaney 1987). The profile of the furnace temperature is shown in Figure 1.

In preparing CuInSe_2 compound, the temperature was initially raised to 200°C and kept for 5 h to allow indium and selenium to diffuse into copper. The temperature was then raised to 900°C . After 2 h of waiting time, the furnace was rocked for 72 h to ensure proper mixing and sample homogeneity. The ramp-up and ramp-down rates of temperature were set at $2^\circ\text{C}/\text{min}$ and rocking frequency was set at 3 cycles/min with 45° angle. The furnace temperature profile is shown in Figure 2.

The SnSe and CuInSe_2 compounds were taken out from the ampoules and were ground into fine powders

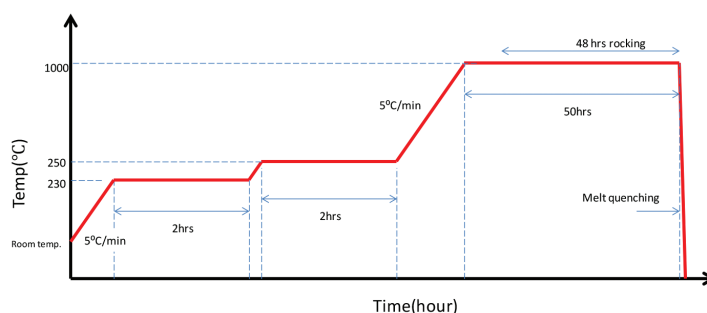


FIGURE 1. Temperature profile of the rocking furnace to prepare the SnSe compound

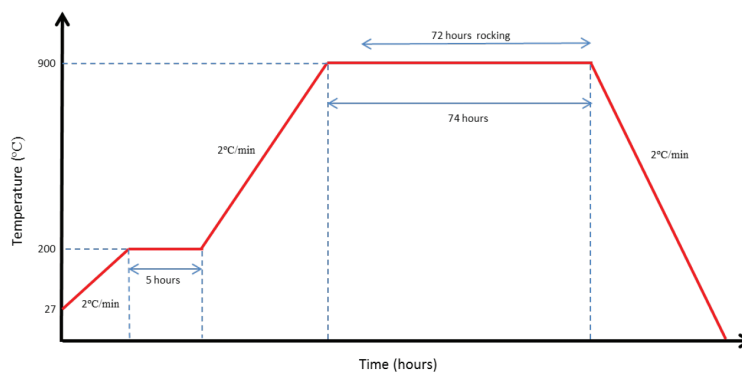


FIGURE 2. Temperature profile of the rocking furnace to prepare the CuInSe_2 compound

for XRD analysis. The XRD patterns were measured on an XPERT-PRO X-ray diffractometer with $\text{Cu K}\alpha$ (1.54056 \AA). After confirming their structures by XRD, the prepared compounds were then used as source materials.

Properly cleaned microscopic glass slides were used as substrates. Substrate cleaning procedure was described earlier (Sabli et al. 2013). Thin films of SnSe and CuInSe_2 were deposited by a thermal vacuum evaporator (Model Edwards AUTO 306) on pre-cleaned glass substrates that were kept at room temperature. A molybdenum boat was used to evaporate the source material. The substrate was kept 14 cm above the boat. Synthesized SnSe powder (0.10 g) was put in the molybdenum boat and the pressure inside the vacuum chamber was pumped down to $2.5 \times 10^{-4} \text{ Pa}$. Prior to deposition, the compound was pre-heated for 1 h at a temperature lower than the compound melting point. By gradually increasing the applied current, the material in the boat turned to molten state and then evaporated. CuInSe_2 thin film was prepared by the same procedure described for SnSe .

The films were characterized by XRD, using the diffractometer described above. The surface morphology of the films was observed by a field emission scanning electron microscope FESEM (Nova NanoSEM 230). The atomic compositions of the as-deposited thin films were investigated by EDX (Oxford Instruments model 7353) attached to the FESEM. A high surface profilometer (Ambious-Tech XP-200) was used to measure thin film thickness. Optical absorption spectra were measured in the wavelength range 200–800 nm on a Shimadzu UV-VIS-NIR spectrometer.

RESULTS AND DISCUSSION

X-ray diffraction patterns for SnSe and CuInSe_2 compounds. The resulting SnSe and CuInSe_2 compounds were originally obtained as a single ingot and granules, respectively. The powder XRD patterns for both synthesized SnSe and CuInSe_2 compounds are shown in Figures 3 and 4. The XRD peaks were compared with the standard data for SnSe (JCPDS Card number: 98-009-1204) and CuInSe_2 (JCPDS Card number: 98-005-0070). The XRD pattern of the

synthesized SnSe powder, Figure 3, shows that the peaks are well matched with the reference card and the (111) plane emerges as the strongest orientation in accordance with earlier literature (Haas et al. 1993). The complete absence of any elemental Sn and Se peaks in the XRD pattern indicates that the sample powder is a single phase of SnSe compound with no un-reacted Sn and Se precipitates. No other non-stoichiometric compounds were detected.

The XRD pattern of the synthesized CuInSe_2 powder, Figure 4, shows that the peaks are well matched with the reference card and the (112) plane emerges as the strongest orientation, in accordance with earlier literature (Muller et al. 2006). The absence of any peaks corresponding to elemental Cu, In or Se in the XRD indicates that the sample powder is a single phase of CuInSe_2 compound free of unreacted elements and other non-stoichiometric compounds.

The high temperature reaction method, using combination of evacuated sealed ampoule at comparatively low pressure of the order of 10^{-1} Pa without inert gas, programmed temperature control and rocking furnace, has successfully yielded stoichiometric source materials for vacuum thermal deposition.

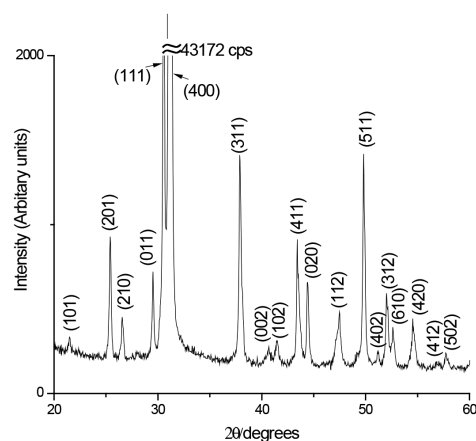
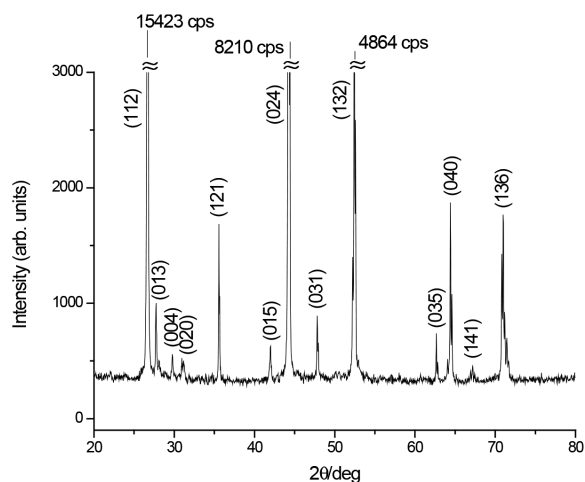
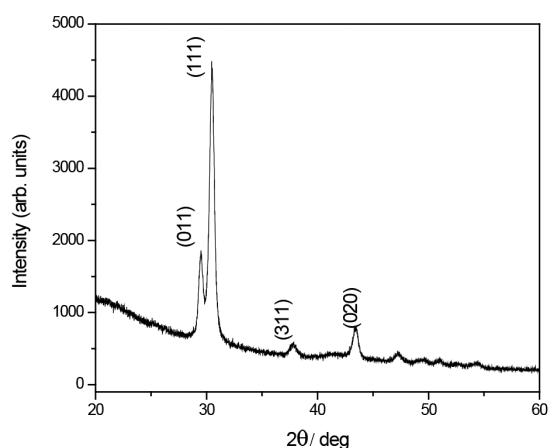


FIGURE 3. XRD pattern for synthesized SnSe powder

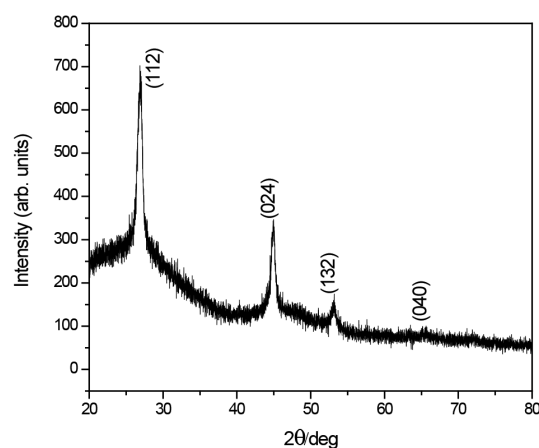
FIGURE 4. XRD pattern for synthesized CuInSe₂ powder

X-RAY DIFFRACTION PATTERNS FOR SnSe AND CuInSe₂ THIN FILMS

The XRD patterns recorded for the as-deposited SnSe and CuInSe₂ thin films are shown in Figure 5. All peaks can be assigned based on the corresponding crystal structure of each compound, SnSe and CuInSe₂ and the assigned indices are presented in the figures. Each of the SnSe and the CuInSe₂ thin films exhibited only a single phase with 1:1 and 1:1:2 stoichiometric ratios, respectively. The SnSe film showed an orthorhombic space group Pnma (a: 11.6 Å, b: 4.2 Å, c: 4.5 Å), whereas the CuInSe₂ film showed a tetragonal space group I-42d (a: 5.8 Å, c: 11.6 Å) crystal structure. The peak intensities of the CuInSe₂ thin film are ten times lower than those of the SnSe film. The thickness values for the SnSe and the CuInSe₂ thin films prepared using 0.10 g of powder were 571 and 429 nm, respectively, as measured by profilometry. Although the films showed comparable thicknesses, the peak intensities of the films showed large differences. The CuInSe₂ film exhibited poor crystallinity.



(a)



(b)

FIGURE 5. XRD patterns for thin films deposited on glass substrates (a) SnSe and (b) CuInSe₂

The grain size (G) values for the films were calculated using the Scherrer's formula:

$$G = (0.9\lambda) / (\beta \cos\theta), \quad (1)$$

where λ is the wavelength of CuK α (1.5405 Å), β is the full width at half maximum intensity of the peak and θ is Bragg's angle of the corresponding diffraction peak. The measured inter-planar distance (d-spacing) values for both SnSe and CuInSe₂ films, together with corresponding standard values, are shown in Tables 1 and 2. Since the FWHM values also give information about crystallite quality, large FWHM values suggest that the films, especially CuInSe₂ film, involve imperfections and disorders. As described above, the weak intensities of the peaks for the CuInSe₂ film indicate poor crystallinity.

EDX FOR SnSe AND CuInSe₂ THIN FILMS

Energy dispersive X-Ray analysis (EDX) spectra were measured for SnSe and CuInSe₂ thin films. Five different points were measured on each film, each point having a scan area of 1 $\mu\text{m} \times 1 \mu\text{m}$. The averaged atomic % values of each element with standard deviations of the films are shown in Table 3. Since the standard deviations of the films are small, both as-grown films show homogeneous compositions. For SnSe film, the average at% values of the constituent elements, Sn: 43.35 \pm 0.64% and Se: 56.65 \pm 0.64%, indicate nearly stoichiometric level (50:50). For CuInSe₂ film, the measured average at% values of the Cu, In and Se elements, 22.32 \pm 0.16%, 24.30 \pm 0.27% and 53.39 \pm 0.17%, respectively. Although these results are almost consistent with the XRD results, the atomic contents still deviate from the stoichiometric level (25: 25: 50). The difference indicates an existence of tiny parts of non-reacted elements and/or amorphous phase. The Se contents of both films exceed the stoichiometric level. Free unreacted amorphous form Se may be present in the film.

TABLE 1. Comparison between the XRD results of SnSe thin film and JCPDS ref. card #98-009-1204

2 θ (°)	d-spacing (Å)		β (°)	Crystallite size (nm)	(hkl)	Compound
	Observed	JCPDS				
29.42	3.03	3.03	0.57	15.7	(011)	SnSe
30.35	2.93	2.93	0.57	15.7	(111)	SnSe
37.67	2.39	2.38	0.57	16.1	(311)	SnSe
43.54	2.08	2.08	0.57	16.4	(020)	SnSe

TABLE 2. Comparison between the XRD results of CuInSe₂ thin film and JCPDS ref. card #98-005-0070

2 θ (°)	d-spacing (Å)		β (°)	Crystallite size (nm)	(hkl)	Compound
	Observed	JCPDS				
26.77	3.32	3.34	1.04	8.2	(112)	CuInSe ₂
44.24	2.01	2.04	1.04	8.6	(024)	CuInSe ₂
53.01	1.72	1.74	1.04	8.9	(132)	CuInSe ₂
65.15	1.43	1.45	1.04	9.5	(040)	CuInSe ₂

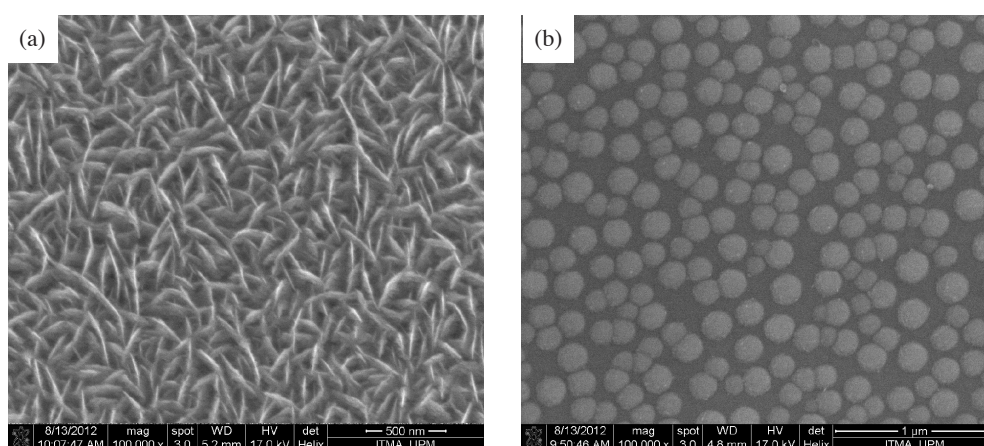
FESEM FOR SnSe AND CuInSe₂ THIN FILMS

FESEM micrographs for SnSe and CuInSe₂ thin films are shown in Figure 6. Figure 6(a) shows that the SnSe film consists of many stacked flakes, with length values ranging from 151 to 351 nm, and thickness values ranging from 28 to 35 nm, perpendicular to the substrate surface. Figure 6(b) shows that the CuInSe₂ film consists of isolated spherically-shaped particles, with diameter ranging from 84 to 197 nm. Both films showed clear shapes which can be directly measured. For the CuInSe₂ film, each particle is isolated on the substrate and does not form continuous interconnected layer. As such, the film would not be suitable for use in photo electrodes and other applications. This can be improved by the proper selection of the substrate, with relatively high surface energy enough to interact with the CuInSe₂.

OPTICAL PROPERTIES OF SnSe AND CuInSe₂ THIN FILMS

The uv/visible spectra were measured, in the range of 200 - 800 nm, for the as-deposited SnSe and CuInSe₂

thin films. Figure 7(a) and 7(b) shows plots of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) for both SnSe and CuInSe₂ films, respectively, where α is the measured absorption coefficient calculated from the experimental value of absorbance (A) and measured thickness (t in nm unit) using the relation $\alpha = 2.303A/t$ (Singh et al. 2011). The $2.303A/t$ is a derived equation from $\alpha t = 2.303 \log I/I_0$, where the relationship between incident intensity and the penetrating light intensity is given by $I = I_0 e^{-\alpha t}$ (Mustafa 2013). The linearity in the relationship of $(\alpha h\nu)^2$ vs. ($h\nu$) for both films indicates that both films have direct band gaps. Since measured thickness values by high surface profilometer (Ambious-Tech XP-200) was 571 and 429 nm for SnSe and CuInSe₂ thin films, the estimated direct optical band gap (E_g) were 1.23 and 1.51 eV, respectively. The value for SnSe is consistent with the reported value (1.21 eV) (John et al. 1994). On the other hand, the band gap for CuInSe₂ values is larger than literature value (1.41eV) (Sakata & Ogawa 2000). From the XRD and the absorption measurements, the CuInSe₂ thin film shows larger FWHM value and larger absorption coefficient than the SnSe film,

FIGURE 6. FESEM micrographs for thin films for (a) SnSe and (b) CuInSe₂

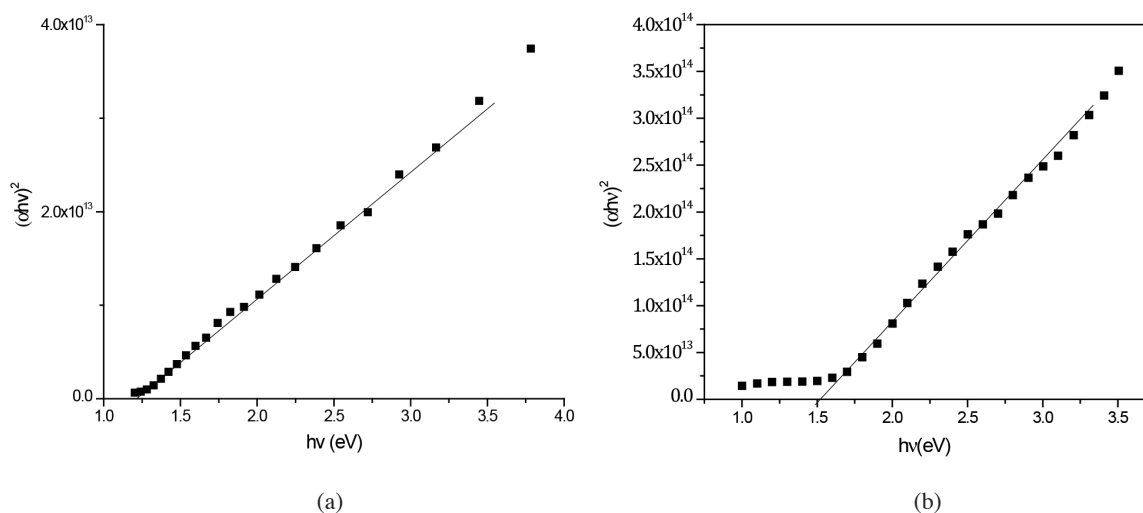


FIGURE 7. Optical absorption spectra showing plots of $(\alpha hv)^2$ vs. photon energy for thin films for (a) SnSe and (b) CuInSe₂

which indicates that the crystallinity of the CuInSe₂ thin film is poorer than that of the SnSe film. The fact that band gap value increases with increased disorder, as the results show here, is well documented (Banerjee et al. 2000; Hilal et al. 2009; Lippens & Lannoo 1989; Zyoud et al. 2013). Vacuum deposition for ternary compounds is presumably more difficult to control than binary compounds. To prepare high quality CuInSe₂ thin film we need to control deposition parameters more precisely, namely evaporation temperature, evaporation speed, substrate temperature and base pressure.

ELECTRICAL PROPERTIES OF SnSe AND CuInSe₂ THIN FILMS

The sheet resistance measurements yield valuable information about conduction mechanism in thin film semiconductors. The electrical properties of the SnSe and CuInSe₂ thin films were studied at room temperature Hall measurements in van der Pauw configuration. The values of sheet resistances for SnSe and CuInSe₂ were $1.99 \times 10^2 \Omega\text{cm}$ and $9.62 \times 10^{-3} \Omega\text{cm}$, respectively, which is in the range of semiconductor at room temperature which is generally $\sim 10^{-2}$ to $10^9 \Omega\text{cm}$ (Shimura 1989). Summary of Hall effects measurement is shown in Table 4. The positive sign of the Hall coefficient confirms the p-type conductivity of both SnSe and CuInSe₂ films. p-type is typical conductivity for SnSe and CuInSe₂ film and totally consistent with earlier report (Fray & Lloyd 1979; Indirajith et al. 2010). The fact that the value of sheet resistant for SnSe and CuInSe₂ is within the semiconductor range and p-type behavior indicates the potential of this materials to be used as absorber material in thin film hetero-junction solar cells.

CONCLUSION AND FUTURE WORK

SnSe and CuInSe₂ compounds were prepared using a modified method by combining evacuated ampoule and

rocking furnace, for the first time. The compounds were then used as source materials to prepare thin films of SnSe and CuInSe₂. The SnSe film consists of many stacked flakes, whereas the CuInSe₂ consists of isolated spherical-shaped particles. Both films were single phased with polycrystalline nature. The XRD results were consistent with earlier literature and with standards; The SnSe showed an orthorhombic structure, while the CuInSe₂ was a tetragonal. Thus the modified preparation system to prepare the compounds described here could be a future method of choice to produce source materials suitable for vacuum thermal evaporation manufacturing of binary and ternary metal chalcogenide thin films. Using this technique in preparing quaternary metal chalcogenide compounds, as source materials, is also worth for future study.

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