Effect of [Cu]/[Cu+In] molar ratios on the growth and physical properties of CuInS₂ nano-particles using non-vacuum method

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Abstract
In this study, CuInS₂ nano-particles were prepared in an ultrasonic bath using the non-vacuum method. The X-ray diffraction (XRD) patterns of samples revealed that the samples are the tetragonal CuInS₂ phase with a highly (112) preferential orientation. With an increase in [Cu]/[Cu+In] molar ratio in precursor solution, the XRD patterns of the samples indicate that the samples are tetragonal CuInS₂ phase, except that the diffraction peaks were slightly shifted to higher angles. The [Cu]/[Cu+In] molar ratio of samples increased with an increase in [Cu]/[Cu+In] molar ratio in precursor solution. No apparent sulfur deficits were observed in samples using energy dispersive analysis of X-ray (EDAX). With [Cu]/[Cu+In] molar ratio in samples of greater than 0.50, the samples are p-type semiconductors while with [Cu]/[Cu+In] molar ratio in samples of less than 0.47, the samples are n-type semiconductors. CuInS₂ samples with an average diameter of 20 nm were observed using transmission electron microscope (TEM). The direct energy band gaps of samples were in the ranges of 1.33-1.57 eV obtained using UV-vis-NIR spectrophotometer.

Keywords: CuInS₂, spin-coating, nano-particles, solar cells

1. Introduction
Chalcopyrite I-III-VI semiconductor compounds (I=Cu, Ag; III=Al, In, Ga; VI=S, Se, Te) have been developed for use in high efficiency thin film solar cells [1]. CIS (CuInS₂) is an interesting photo-absorber material in I-III-VI thin film solar cells due to their high-absorption coefficient, suitable band gaps, good radiation stability, and easy conversion of n/p carrier type [2]. The direct energy band gap in the range of 1.3-1.5 eV and an absorption coefficient of around 10⁶ cm⁻¹ for CIS samples is reported, which is suitable for the solar energy conversion. The preparation of low-cost ternary chalcopyrite CIS solar cells with high solar to electricity efficiency has thus received considerable industrial interest.

The conversion efficiency of solar to electrical power of 14% has been reported for the lab-scale CIS solar cell [3]. Various methods for the preparation of I-III-VI thin films on substrates have been reported, such as evaporation [3] and radio-frequency (RF) sputtering [4]. To address the production cost of CIS devices, many efforts have been made for the low cost approach of the deposited CIS material on substrates. Reports of non-vacuum, solution-based approaches include a nanoparticle solution based technique [5], spray pyrolysis, [6], chemical bath deposition [7] and electrodeposition [8].

In contrast to the physical and chemical vapour deposition techniques, chemical synthesis method is a simple, inexpensive and non-vacuum technique in which the molar ratios of the composition of sample can be controlled by adjusting their molar ratios in the precursor solution. In the present work, we synthesized the CIS nano-particles using the convenient chemical synthesis method. The microstructures, physical, electrical and optical properties of CIS samples on substrates are examined as a function of [Cu]/[Cu+In] molar ratio in precursor solutions.

2. Experimental Details

2.1 Synthesis of the CIS nano-particles

In this study, the CIS nano-particles were prepared using the copper nitrate [Cu(NO₃)₂.2.5H₂O], indium nitrate [In(NO₃)₃.5H₂O] and thioacetamide (CH₃CSNH₂, TAA) as the precursors in a 20 ml ethanol bath. The reaction solution was put into an ultrasonic bath for 4.5 h with the temperature kept at 65°C. The copper to indium ratio [Cu]/[Cu+In] in reaction solution bath was verified for the preparation of CIS nona-particles. After reaction, the CIS powders were annealed in a quartz tube with the annealed temperature kept at 450°C.

2.2 Deposition of CIS thin films

The PEG (poly ethylene glycol) was mixed well with the CIS nano-particles after thermal treatment. The films were deposited on glass substrates using a spin-coater. Then the films were placed on a 90°C oven for 24 h in order to eliminate the volatile solvent. The CIS thin films and sufficient element S were put in a closed container made of Al₂O₃. Final the thin films on substrates was carrier out using the sputurification process with 450, 500 for 90 min and 550°C and thermal treatment time of 20, 40, 60 and 90 min, respectively.

2.3 Characterization of CIS nano-particles and thin films

The crystallographic study of samples on glass substrates was conducted using an X-ray diffraction (Siemems D5005) with CuKα (λ = 1.5405 Å) radiation. The XRD patterns of samples were recorded in the 20 range of 10° to 90°. The scan rate was set to 3° min⁻¹ in order to increase the signal-to-noise ratio. The microstructure of samples was investigated using a transmission electron microscope (TEM, JEOL JEM-1230). The surface microstructures of the samples were also studied using a field-emission scanning electron microscope (FE-SEM, JEOL JSM 6700F). The compositions of the samples on glass substrates were analyzed using a scanning electron microscope (SEM, Hitachi S-3000N) equipped with energy dispersive analysis of X-ray (EDAX). The mobility, resistivity, and carrier concentrations of the samples were measured using room temperature Hall measurements (Ecopia Model HMS-3000) with a magnetic flux of 0.51 T. The transmittance/reflectance spectra of the samples were measured using a UV-Vis-NIR spectrophotometer with an integrating sphere (JASCO Model V-670) in the wavelength range of 300-1600 nm at room temperature.

3. Results and Discussion

The CIS nano-particles were synthesized using solution growth technique. The effect of [Cu]/[Cu+In] molar ratio in precursor solution on the physical properties of CIS nano-particles is examined. The [Cu]/[Cu+In] molar ratios in precursor solution were kept at 0.57, 0.52, 0.50, 0.49, 0.47, 0.46, 0.44 and 0.41, respectively. Figure 1 shows the XRD pattern of the CIS nano-particles with various [Cu]/[Cu+In] ratios in precursor solutions after annealed at 450°C for 1 h. The XRD peaks at 27.93°, 46.52° and 55.15° correspond to (112), (200), (204) and (312), (116) crystal phases of the CIS (JCPDS card no. 27-0159) phase. All samples are the polycrystalline tetragonal CIS phase. With the [Cu]/[Cu+In] molar ratio in precursor solution of greater than 0.56, the peaks...
samples shifted to higher angle. Increasing amount of Cu in precursor solution (sample (a)-(h)). The ratio of [Cu]/[Cu+In] in solution bath increased from 0.41 to 0.57 (samples (h)→(a)), the peaks of XRD patterns of samples shifted to higher angle.

The [Cu]/[Cu+In] and 2[S]/[Cu+3In] molar ratios obtained from XRF (X-ray fluorescence) analysis for CIS nano-particles as a function of [Cu]/[Cu+In] molar ratio in precursor solution are shown in figure 2. The molar ratios of [Cu]/[Cu+In] and 2[S]/[Cu+3In] were in the ranges of 0.46-0.64 and 0.92-0.80, respectively. With an increase in the [Cu]/[Cu+In] molar ratio in precursor solutions, the [Cu]/[Cu+In] molar ratio in CIS nano-particles also increased. The XRF analysis shows that sample (g) is nearly stoichiometric CIS nano-particles. The 2[S]/[Cu+3In] molar ratios in all CIS nano-particles are less than 1.0, which indicates some sulphur deficits in the CIS nano-particles.

The crystal phase and morphology of the CIS nano-particles with the [Cu]/[Cu+In] molar ratio kept at 0.50 in precursor solution was studied using a transmission electron microscope (TEM). The TEM image and corresponding selected area electronic diffraction (SAED) patterns of the sample with [Cu]/[Cu+In] molar ratio in precursor solution kept at 0.50 are shown in figure 3. The TEM image of nano-particles with [Cu]/[Cu+In] molar ratio in precursor solution kept at 0.5 shows relatively small crystals with size distribution from 10 to 30 nm. The SAED pattern of CIS nano-particles agrees well with the tetragonal CIS phase spots, which is in agreement with the XRD data. Figure 4 shows the XRD patterns of CIS thin films on substrates using the nano-particles obtained from the [Cu]/[Cu+In] molar ratio kept at 0.47 in precursor solution after the sulfurization process with various annealing temperature (450, 500 and 550°C) and time (20, 40, 60 and 90min). The XRD patterns of sample show that all samples are the tetragonal CuInS₂ phase. The higher intensity of peaks in XRD patterns for thin films was observed after annealing temperature kept at 550°C and 60min. This is due to that thin films have excellent quality and good crystalline after the high temperature annealed process. Figure 5 shows the surface morphology and cross-sectional image of sample using the nano-particles obtained from the [Cu]/[Cu+In] molar ratio kept at 0.47 in precursor solution after sulfurization at 550°C for 60 min. The SEM image of sample showed island-shaped microstructures. Table 1 shows the molar ratios of [Cu]/[Cu+In], 2[S]/[Cu+3In] and electrical properties of sample obtained using the nano-particles obtained from the [Cu]/[Cu+In] molar ratio kept at 0.47 in precursor solution after various annealing temperature and time. As the results, the sulfurization temperature of 550°C for 60 min to obtain CIS thin films on substrates was employed in this study.

Figure 6 shows the XRD spectra of samples on substrates obtained with various [Cu]/[Cu+In] molar ratios in precursor solution after sulfurization process. Table 2 lists [Cu]/[Cu+In] and 2[S]/[Cu+3In] molar ratios in samples obtained from EDAX analysis. The conduction type, carrier concentration, and mobility of samples on glass substrates were determined using room temperature Hall measurements. With [Cu]/[Cu+In] molar ratio in samples of greater than 0.50, the samples are p-type semiconductors while with [Cu]/[Cu+In] molar ratio in samples of less than 0.47, the samples are n-type semiconductors. The carrier concentration and mobility of samples on substrates were in the ranges of 3.31×10¹⁹ to 8.19×10¹⁸ cm⁻³ and 2.13 to 59.6 cm²/V·s, respectively.

Figure 7 shows the linear dependence of (αhv)² on hv for the samples in this study. The absorption coefficients (α) of samples can be estimated using the Manfacier model [2]. The relationship between the absorption coefficient (α) and the incident photon energy (hv) can be written as:

\[
\alpha(hv) = (hv - E_g)^{\frac{1}{2}}
\]

The direct band gaps of samples obtained from Figure 7 are shown in table 2. The direct band gaps of samples were in the range of 1.33–1.57 eV. Das et al. [9] reported the same results. The direct band gaps of bulk crystalline CIS are in the range of 1.3–1.55 eV [9]. The values of energy band gap for samples (a)-(h) are close to the value reported for bulk crystalline CIS.

Conclusions

In this study, chalcopyrite CIS nano-particles were prepared using solution growth technique. The crystals size distribution of CIS nano-particles was in the range of 10 to 30 nm. The XRD patterns of samples show that the samples are the polycrystalline tetragonal CIS phase. From the XRD, FE-SEM and electrical properties results, the sulfurization temperature and time kept 550°C for 60 min is an optimal parameter for the preparation of CIS thin films on substrate. With [Cu]/[Cu+In] molar ratio in solution bath less than 0.47, the samples are n-type semiconductors. With [Cu]/[Cu+In] molar ratio in solution bath greater than 0.50, the samples are p-type semiconductors. The direct energy band gaps of the samples were in the ranges of 1.33–1.57 eV, respectively.

Acknowledgements

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References


Figure 1 XRD patterns of CIS nano-particles prepared with various [Cu]/[Cu+In] molar ratios in precursor solutions. (a) 0.57, (b) 0.52, (c) 0.50, (d) 0.49, (e) 0.47, (f) 0.46, (g) 0.44 and (h) 0.41.
Figure 2 Molar ratios of [Cu]/[Cu+In] and 2[S]/[Cu+3In] for samples as functions of the [Cu]/[Cu+In] molar ratio in precursor solutions.

Figure 3 TEM images of CIS nano-particles (a) in 5000K(X) and (b) the selected-area electron-diffraction pattern of the CIS nano-particles.

Figure 4 XRD patterns of samples with [Cu]/[Cu+In] molar ratio of 0.9 in precursor solutions after various sulfurization processes. (I) 450°C for 90 min, (II) 500°C for 90 min, (III) 550°C for 90 min, (IV) 550°C for 60 min, (V) 550°C for 40 min and (VI) 550°C for 20 min of sample (e).

Figure 5 (a) SEM images of CIS films and (b) the cross-section image of sample (e).

Figure 6 XRD patterns of CIS samples with various [Cu]/[Cu+In] molar ratios in precursor solutions annealed at 550°C for 60 min: (a) 0.57, (b) 0.52, (c) 0.50, (d) 0.48, (e) 0.47, (f) 0.46, (g) 0.44 and (h) 0.41.

Figure 7 Plots of $\alpha h\nu$ versus $hv$ of samples.

Table 1 Physical properties of CIS prepared with various parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parameter</th>
<th>Atomic ratios of CuInS$_2$ thin films</th>
<th>Resistivity</th>
<th>Carrier concentration</th>
<th>Mobility</th>
<th>Direct $E_g$</th>
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<td></td>
<td></td>
<td>(from EDS analysis)</td>
<td>$\Omega$cm</td>
<td>$\mu$cm$^2$/V-s</td>
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<tr>
<td>(I)</td>
<td>450°C-90min</td>
<td>0.56 [Cu]/[Cu+In] 1.07 [2S]/[Cu+3In]</td>
<td>$3.24\times10^2$</td>
<td>$1.30\times10^7$</td>
<td>27.0</td>
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<tr>
<td>(II)</td>
<td>500°C-90min</td>
<td>0.53 [Cu]/[Cu+In] 1.18 [2S]/[Cu+3In]</td>
<td>$5.11\times10^2$</td>
<td>$6.27\times10^8$</td>
<td>24.0</td>
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<td>(III)</td>
<td>550°C-90min</td>
<td>0.56 [Cu]/[Cu+In] 1.12 [2S]/[Cu+3In]</td>
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<td>$3.32\times10^7$</td>
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<td>(IV)</td>
<td>550°C-60min</td>
<td>0.53 [Cu]/[Cu+In] 1.17 [2S]/[Cu+3In]</td>
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<td>$7.43\times10^7$</td>
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<td>(V)</td>
<td>550°C-40min</td>
<td>0.52 [Cu]/[Cu+In] 1.18 [2S]/[Cu+3In]</td>
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<td>(VI)</td>
<td>550°C-20min</td>
<td>0.58 [Cu]/[Cu+In] 1.13 [2S]/[Cu+3In]</td>
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<td>$6.27\times10^7$</td>
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Table 2 Physical properties of CIS thin films on substrates after sulfurization at 550°C for 60 min.

<table>
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<tr>
<th>Sample</th>
<th>[Cu]/[Cu+In] molar ratio in precursor solution</th>
<th>Atomic ratios of CuInS$_2$ thin films (from EDS analysis)</th>
<th>Resistivity</th>
<th>Carrier concentration</th>
<th>Mobility</th>
<th>Direct $E_g$</th>
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<tr>
<td></td>
<td>[Cu]/[Cu+In]</td>
<td>[2S]/[Cu+3In]</td>
<td>$\Omega$cm</td>
<td>$\mu$cm$^2$/V-s</td>
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<td>(a)</td>
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<td>(d)</td>
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<td>0.53</td>
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<td>$1.75\times10^{16}$</td>
<td>59.6</td>
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<tr>
<td>(e)</td>
<td>0.47</td>
<td>0.53</td>
<td>1.17</td>
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<td>$7.43\times10^{16}$</td>
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<td>(g)</td>
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<td>$4.88\times10^7$</td>
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