CuInS₂ Ternary Compound as Absorption Layer for Solar Cell Fabrication

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Abstract

Copper indium disulphide, CuInS₂, is a promising absorber material for thin film photovoltaic which has recently attracted considerable attention due to its suitability to reach high efficiency solar cells by using low cost techniques. In this work CuInS₂ thin films have been deposited by chemical spray pyrolysis onto glass substrates at ambient atmosphere, using different [Cu]/[In] ratio in the aqueous solutions at substrate temperature 300°C ± 5 and different annealing temperatures. Structural and optical properties of CIS films were analyzed by X-ray diffraction, and optical spectroscopy. Sprayed CIS films are polycrystalline with a chalcopyrite structure with a preferential orientation along the 112 direction and no remains of oxides in higher ratio were found after spraying in suitable conditions. X-ray microanalysis shows that a chemical composition near to stoichiometry can be obtained. An optical properties showed this material have a direct band gap and the energy band in the range of about 1.4 - 1.61 eV at different ratio was found for sprayed CIS thin films.

Keywords

CuInS₂ Ternary Compound

Article info

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Introduction
Solar cell technologies using Cu-III-VI\textsubscript{2} chalcopyrite semiconductors have made rapid progress in recent years. The properties, such as high optical absorption coefficient and band gap energy of 1.5 eV, have raised researchers’ interest in CuInS\textsubscript{2} thin films used as an absorber layer in solar cells [1]. In the present work, These chalcopyrite compounds have great potential for thin-film solar cell applications. That can be predicated theoretically that homojunction fabricated using this material can yield an efficiency of 27% to 32% [2]. Efficiencies more than 12% have been reached with an Mo/CuInS\textsubscript{2}/CdS/ZnO cell structure [3].

Ternary chalcopyrite semiconductors, CuInS\textsubscript{2} (CIS) may be the most promising material for photovoltaic applications. CuInS\textsubscript{2} has been predicted theoretically to have the highest conversion efficiency among chalcopyrite solar cells. This is due to the suitable band gap and direct band gap of 1.5 eV which perfectly matches the solar spectrum for energy conversion and to the large absorption coefficient of almost \(10^4\) \(\text{Cm}^{-1}\). Furthermore, the material does not contain toxic Ga or Se, this may have an advantage in comparison with the frequently studied CuInS\textsubscript{2} and CIGS. Several methods of depositing CIS polycrystalline thin films, chemical spray pyrolysis (CSP) used in the present work to prepare CuInS\textsubscript{2} as absorber layer. One of the major Problems of this class of materials is the control of the stoichiometry, control of the excess copper content and of the copper to indium ratio. Because of the large different in the vapor pressures of copper, indium.

Experimental
Copper indium sulphide (CIS) films were deposited by spray pyrolysis onto glass substrates from aqueous solutions of copper chloride, indium chloride and thiourea using compressed nitrogen (N\textsubscript{2}) as the carrier gas. The copper/indium ratio (Cu/In) in the solution was varied between 0.5 and 1.5 and the sulphur/copper ratio (S/Cu) was fixed at 5. The solution was sprayed in air onto glass substrates in the dimension (25x25x1.2 mm\textsuperscript{3}) at substrate temperatures 300 °C ± 5 and using fixed volume at all ratios is 50 ml. Films thickness was measured by The Weighting Method and found to be in the range of 800–1200 nm thickness. The structural properties of these films were characterized by X-ray diffraction using (Shimadzu XRD 6000). XRD patterns in the 2θ rang (20-50) The XRD spectra reveal that all obtained films sprayed at substrate temperatures equal to 300 °C have a polycrystalline with chalcopyrite structure compared with (JCPDS File №. 027-0159) with a preferred orientation along (112) direction. Optical properties were monitored by SHIMADZU Spectrophotometer type (UV-1650 PC) optimized for the UV–VIS range. Absorbance spectra of the CIS films measured in the range of 300–900 nm at room temperature and the absorption coefficient versus photon energy was calculated. All the films exhibit high absorbance in the studied UV–Vis range.

Results and Discussions
1. Structural Properties
CuInS\textsubscript{2} films are prepared using (CSP) techniques in different Cu/In ratios started in (0.5, 1, 1.5, ) [S]/[Cu] ratio kept at 5 in the solution, and deposited on glass substrate at 300°C. Grain size of the films at different ratio was calculated using the debye- Scherrer formula, and compared with (JCPDS) standard card № (27-0159). Grain size computed at different Cu/In ratio and different annealing temperature present in table (1). XRD pattern for these ratios are presented in fig (1). XRD pattern of the film sprayed at Cu/In ratio equal (0.5) present in fig. (1-a) indicates this ratio "In-rich" in the film and the pattern show us non-stoichiometry caused poor crystallinity for this film, used different annealed temperature (250, and 350°C) to the film. These results (lattice parameter
and grain size) of this ratio are not consistent with the results of the researcher Theresa et.al. [4], when the ratio is 1 which refers to the equivalent ratio of (Cu) to the (In) in the solution present in fig (1-b) show to as improvement in the crystal structure, and this was approaching to the practical value (observed value, d, a, c) from theoretical values form (JCPDS) card these result are closer than when annealing sample at different temperature (250,350°C). As can be seen the peaks with high intensity Sites along (112) plane this is preferential orientation at θ = 27.95° these result agree with the result of Theresa et.al [4] and disagree with the result of Naua et.al [5]. The XRD pattern show as in fig. (1-c) at Cu/In ratio equal 1.5, The crystalline structure at this ratio have a big improvement with increasing Cu/In ratio, and we can observed a highest intensity for preferential orientation along (112) and this pattern shows lower or smallest peaks corresponding to the plane (004/200), (204/220). This result disagreement with the result of Mahanubhay et.al [6] and with the result of Peza et.al. [7].

Table (1) show the grain size at different ratio

<table>
<thead>
<tr>
<th>Cu/In</th>
<th>I/Io</th>
<th>Grain size As – dep nm</th>
<th>Grain size Ta = 250 C nm</th>
<th>Grain size Ta = 350 C nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>100</td>
<td>2.75</td>
<td>4.49</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>8.74</td>
<td>6.83</td>
<td>11.55</td>
</tr>
<tr>
<td>1.5</td>
<td>100</td>
<td>45.11</td>
<td>45.08</td>
<td>47.13</td>
</tr>
</tbody>
</table>

Figures (1): showed XRD pattern for CuInS$_2$ at different CuInS$_2$ ratio a- Cu/In=0.5, b- Cu/In=1, and c- Cu/In=1.5

2. Optical Characterization

Absorbance spectra of the CIS films were also measured using Shimadzu UV-VIS – NIR spectrophotometer type (UV-1650PC) in the range of 300–900 nm at room temperature and the absorption coefficient versus photon energy was calculated. All the films exhibit high absorbance in the studied UV–Vis range. The energy of the band gap, $E_g$, was
calculated from the transmission spectra using the following relationship.

\[(\alpha h\nu)^2 = A(h\nu - E_g)\]

Fig. (2) shows the optical Transmission T% as a function of the wavelength for the thin films with Cu/In ratios of 0.5, 1 and 1.5. For the photon energy range shown in Fig. (2-b,c,d), \(\alpha\) reaches value higher than \(10^4\) cm\(^{-1}\). This relatively high absorption coefficient is very important because the spectral dependence of \(\alpha\) drastically affects the solar conversion efficiency. This result agree at \([\text{Cu}]/[\text{In}] = 1\) with result of Peza et.al. [7]. The inset shows the representation of \((\alpha h\nu)^2\) versus \(h\nu\) used for the calculation of the energy gap \(E_g\). The films exhibit direct transitions corresponding to a band gap \(E_g\) in the range of \((1.4 - 1.61)\) eV. Which is in good agreement with the value of \((1.3 \text{ and } 1.43)\) for the CIS thin film prepared by spray pyrolysis Bouzouita et.al. [8].

**Conclusion**

The studies reported here show that it is possible to prepare CIS films using spray pyrolysis technique in ambient atmosphere using compressed \(N_2\) as carrier gas. Sprayed CIS films exhibit a chalcopyrite structure with a preferred orientation in the (112) direction. Structural and optical properties of sprayed films depend on the fabrication conditions, in particular on the Cu/In ratio in the starting solution and annealing temperature.

Films sprayed using solutions in which the copper/indium ratio is 0.5 show no significant change in their structural and optical properties. Films prepared using Cu/In ratio of 0.5 at 300 °C are of poor optical quality and have poor crystallinity, therefore we have focused on solutions with 1.5 \([\text{Cu}]/[\text{In}]\) at 300 °C. It was found that the uniformity, growth rate and adhesions of the films depend strongly on...
the substrate temperature, spray rate and solution concentration.

References