Review Paper:

Quaternary thin films: A review

Ho S.M.
Faculty of Science, Technology, Engineering and Mathematics, INTI International University, Putra Nilai, 71800, Negeri Sembilan, MALAYSIA
soonmin.ho@newinti.edu.my

Abstract
Quaternary thin films were reported for use as the photo absorber in solar cells because of direct band gap and high optical absorption coefficient. In the past few years, there were a number of reports on the properties of thin films prepared by different deposition methods. Characterization of thin films was reported by various researchers in order to study of materials properties especially suited to solar cell applications.

Keywords: Quaternary Thin films, chemical bath deposition, electrodeposition, solar cell, band gap.

Introduction
Chalcogenide thin films exhibit excellent chemical, electrical and optical properties. Generally, they have been widely used in applications such as lasers devices, optoelectronic devices, photoconductive and photovoltaic cells. In the past few decades, research on photovoltaic cells has been focused on the development of new materials. Up-to-date, the preparation and characterization of chalcogenide thin films can be categorized into three groups namely binary, ternary and quaternary compounds. Examples of binary compounds are ZnS[1-3], CdS[4-6], FeS_2[7,8], $CdTe$[9], Sb_2S_3[10], Bi_2Te_3[11],CuS[12], Cu_2S[13], SnS_2[14], SnS[15],NiS[16,17], $NiSe_2$[18], $NiSe$[19],$ZnSe$[20,21], Bi_2S_3[22], $SnSe$[23,24], $PbSe$[25,26], PbS[27, 28], MnS[29,30] and Cu_2Te[31]. Meanwhile, Cu_4SnS_4[32-34], $CdSe_{0.6}Te_{0.4}$[35], $CdIn_2S_4$[36], $CdS_{1-x}Te_x$[37], $SnS_{0.5}Se_{0.5}$[38], $CuInS_2$[39], $Hg_xCd_{1-x}S$[40], $CdMnS$[41], $CuInSe_2$[42], $CdZnSe$[43], $Pb_{1-x}Mn_xS$[44], $AgInS_2$[45],Cu_3SnS_4[46], CdS_xSe_{1-x}[47],

$Cd_{0.6}Hg_{0.4}Se$[48], $ZnIn_2S_4$[49] and $Ni_3Pb_2S_2$[50] are examples of ternary metal compounds. In recent years, quaternary thin films system such as I-II-IV-VI semiconductor has attracted attention and was reported for use as the photo absorber in thin film solar cells.

The competitiveness of production cost and band gap energy matching solar spectrum lead to chalcogenide materials are attractive for solar energy conversion. Currently, the types of research done by various scientists are mostly related to the investigation of materials properties especially suited to solar cell applications. In this review paper, quaternary chalcogenide system prepared using different deposition techniques will be discussed.

Overview
Most of the authors have reported Cu_2ZnSnS_4 (CZTS) thin films for the use as the photo absorber in photovoltaic cells. This is because of several reasons such as these materials are low cost, non-toxic constituents, direct band gap and high optical absorption coefficient as high as 10^4 cm^{-1}. In other words, these materials with band gap (Table 1) in the visible region have developed worldwide interest in the field of renewable energy by using various deposition methods including SILAR, electrodeposition, chemical bath deposition, pulsed laser deposition, magnetron sputtering, spray pyrolysis, arrested precipitation technique and electrochemical epitaxial method. The optical absorption studies of the annealed CZTS films were reported by Bwamba Jonah et al[51]. The obtained absorption spectra indicated that annealed films have a high absorbance of light in the visible region.

On the other hand, various deposition conditions could be carried out to produce interesting sets of samples. Xie et al[52] reported that zinc loss caused poorly crystallized form produced in the sputtered films. However, crystallinity of samples could be improved after sulfurization process. In the energy dispersive X-ray analysis results, the As-deposited CZTS films are slightly copper rich and tin poor as reported by Lin et al[53]. However, the contents of copper and tin reduce while the zinc increases in the annealed samples. CZTS was grown on polycrystalline Ag substrates by electrochemical epitaxial method as reported by Zhang et al[54]. Based on the X-ray photoelectron spectroscopy results, they claimed successfully to produce films with approximate ratio 2:1:1:4 of Cu, Zn, Sn and S. In addition, similar results have been obtained from energy dispersive X-ray analysis as well.

In terms of band gap studies, band gap values obtained for the films annealed at 200, 300, 400 and 500 °C were estimated to be 1.94, 1.87, 1.81 and 1.48 eV respectively. The band gap value reduces with increasing annealing temperature up to 500 °C due to decreasing of defects and improvement of quality of CZTS film during the annealing process[55]. On the other hand, the grain size increased from 100 nm to 2000 nm as the annealing temperature was increased from 250 to 400 °C as reported by Mkawi et al[56]. Furthermore, these thin films were smooth, homogeneous and lacked pinholes as indicated in scanning electron microscopy results. It is noteworthy that the obtained experiment findings vary depending on the annealing treatment.

Overall, there are some problems faced by researchers during the deposition of quaternary thin films. First, multiple binary and ternary phases would be obtained in samples which are considered as impurities. Yeh and Cheng[57] reported the preparation of the Ag-Zn-Sn-S quaternary thin films using chemical bath deposition technique. The X-ray diffraction patterns of the samples reveal that tetragonal Ag_2ZnSnS_4 phase with small amount of impurities such asAg_8SnS_6 and SnS can be obtained using TEA as the chelatingagent and deposition temperature kept at 70 °C.

Secondly, sometimes, it is very difficult to control the stoichiometry in thin films. In order to solve this problem, researchers require excellent control over synthesis parameters to get the desired phase of the materials. For example, X-ray diffraction pattern indicates that broad peaks obtained are identified to be (112) and (220) planes of Cu_2ZnSnS_4 as reported by Subramaniam et al[59]. However, the diffraction peaks from (112) and (220) planes of Cu_2ZnSnS_4 coincide with the peaks from (110) and (220) planes which correspond to the ZnS. It means that the presence of impurities such as binary or ternary compounds is very hard to distinguish by using the XRD technique. Currently, Raman scattering with the different excitation wavelengths could help resolve this problem as pointed out by Nguyen et al[68] in their research findings. For example, secondary phases such as Cu_2SnS_3 and ZnS could be identified easily in their thin films.

Thirdly, the majority of quaternary thin films have lower conversion efficiencies than crystalline silicon. So far, thin films solar cell with 8.4% power conversion efficiency is the highest efficiency reported by Shin et al[69] for Cu_2ZnSnS_4 prepared by thermal evaporation as listed in table 2.

Conclusion

The preparation and characterization of quaternary thin films by using various deposition techniques is discussed in this paper. There are a number of literatures reporting that quaternary thin films could be potential in fabricating high-performance and cost-effective solar cells devices with low environmental pollution. In order to further improve the performance of these materials, efforts should be committed to the development of the approaches for forming pure CZTS phase and the detection techniques of secondary phases formed during the deposition of the CZTS thin film. Also, research efforts need to be focused on cadmium-free and selenium-free CZTS solar cell technologies.

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Table 1
Band gap energy of various thin films prepared using various preparation techniques

Thin films	**Deposition method**	**Band gap**
Ag_2ZnSnS_4	Chemical bath deposition[57]	2.08-2.56
Cu_2ZnSnS_4	SILAR[58]	1.51-1.61
Cu_2ZnSnS_4	Chemical bath deposition[59]	1.5
Cu_2ZnSnS_4	Magnetron sputtering & sulfur vapor technique[60]	1.4
$MoBiGaSe_5$	Arrested precipitation technique[61]	1.3
Cu_2CdSnS_4	atom beam sputtering[62]	1.06
Cu_2ZnSnS_4	atom beam sputtering[62]	1.45
$Cu_xAg_{1-x}InS_2$	spray pyrolysis[63]	1.4-1.7
CuInSTe	quenching technique[64]	1.04-1.1
Cu_2ZnSnS_4	Electrochemical deposition [56]	1.53
Cu_2ZnSnS_4	Field assisted chemical spray pyrolysis[51]	1.54
Cu_2ZnSnS_4	Co-electro deposition method[65]	1.51
Cu_2ZnSnS_4	Electrochemical epitaxial[54]	1.5
Cu_2ZnSnS_4	Pulsed laser deposition[66]	1.5
$Cu_2ZnSnSe_4$	Selenisation, magnetron sputtering [67]	0.9

Table 2
Power conversion efficacy for various thin films prepared using different deposition methods

Thin films	Percentage	Reference	Method(s)
Cu_2ZnSnS_4	4.04 %	Xie et al, 2013[53]	sputtering and sulfurization process
Cu_2ZnSnS_4	3.08 %	Peng et al, 2014[60]	sputtering and sulfurization process
Cu_2ZnSnS_4	1.04-2.04 %	Mkawi et al, 2013[56]	Electrochemical deposition
Cu_2ZnSnS_4	8.4 %	Shin et al, 2013[69]	Thermal evaporation
Cu_2ZnSnS_4	6 %	Tsukasa et al, 2012[70]	Open atmosphere chemical vapor deposition

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