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Study on Indium-free and Indium-reduced thin film solar absorber materials for photovoltaic application

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Key words : Sputtering, chalcogenides, optical properties, solar cell.

Abstract : In this report, Indium-free and Indium-reduced thin film materials for solar absorber were studied in order to search alternative materials for thin film solar cell. The films of $Cu_2ZnSnSe_4$ and $CuInZnSe_2$ were deposited using mixed binary chalcogenides powders. From the film bulk analysis result, it is observed that Cu concentration is a function of substrate temperature as well as CuSe mole ratio in the target. Under optimized conditions, $Cu_2ZnSnSe_4$ and $CuInZnSe_2$ thin films grow with strong (112), (220/204) and (312/116) reflections. Films are found to exhibit a high absorption coefficient of 10^4 cm^{-1}. $Cu_2ZnSnSe_4$ film shows a 1.5 eV band gap. On the other side, an increasing of optical band gap from 1.0 eV to 1.25 eV ($CuInZnSe_2$) is found to be proportional with an increasing of Zn concentration. All films have a *p*-type semiconductor characteristic with a carrier concentration in the order of 10^{14} cm^{-3}, a mobility about 10^1 $cm^{2\cdot-1}\cdot s^{-1}$ and a resistivity at the range of 10^2-10^6 Ω·m.

1. Introduction

The first report on the chalcopyrite $CuInSe_2$ (CISe) thin film solar cell [1] have spurred efforts to study chalcopyrite CISe compound physical properties [2]. To date, the CISe-based material with an additional gallium ($CuIn_{1-X}Ga_XSe_2$/CIGSe) is considered to be one of promising materials for the thin film solar cell with cell efficiency toward 20% [3].

Recently, attention to the A^I-B^{III}-C_2^{VI} - A^{II}-B^{VI} systems for Indium-reduced solar cell has grown noticeably since the first report on successful fabrication of $CuInZnSe_2$ (CIZSe) thin films by evaporation-selenization tehcnique and their *I-V* characteristics [4]. The $(CuInSe_2)_X$-$(2ZnSe)_{1-X}$ solid solution has been proven to have a band gap tunability from 1.0 eV ($CuInSe_2$) to 2.67 eV (ZnSe) and possesses a high absorption coefficient (10^4 cm^{-1}) within visible and near infra red [5]. With respect to CISe, it is realized that the presence of zinc (Zn) in the $(CuInSe_2)_X$-$(2ZnSe)_{1-X}$ system possibly will reduce the material cost by reducing partially the expensive indium (In) and lead to an opportunity to fabricate a low cost thin film solar cell. On the other side, based on attempts to find Indium-free better, the exploration of the physical properties of quaternary Cu_2-II-IV-VI_4 single crystals has been initiated. These quaternary compounds are considered to be a novel material for alternative thin film solar cells owing to their being a *p*-type material with band gap energies ranging from 0.96 to 1.63eV [6]. They can be tailored by different combinations of elements from within the group II, IV and VI elements. Several studies have suggested the use of Cu_2-II-IV-VI_4 as an alternative material for solar cells. Ito and Nakazawa reported for the first time the photovoltaic effect of quaternary Cu_2ZnSnS_4 (CZTS) solar cells which employed Zn and Sn as alternatives to In, whereas Matsushita and his co-workers reported the *I-V* characteristics of the *p*--*n* junction of *n*-CdS/*p*-$Cu_2ZnGeSe_4$[7-8]. Only a few works have focused on the growth of device-quality quaternary films and the improvement of the efficiency of quaternary film-based solar cells. In this paper, an alternative approach for growing $CuInZnSe_2$ and $Cu_2ZnSnSe_4$ thin films by means of sputtering technique using binary chalcogenide powder targets is presented and discussed.

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2. Experimental details

In order to prepare a sputtering target for growing stoichiometric $CuInZnSe_2$ thin films, binary chalcogenide powders of CuSe and InSe (each of 99.9 % purity) were initially mixed at 1 : 1 mole ratio.

Addition of 10, 20, 30 and 40 wt. % ZnSe powder to the CuSe and InSe mixture powder were carried out with the purpose of preparing sputtering targets for growing $CuInZnSe_2$ thin films with different Zn concentration.

All powders were milled using a plastic container. The 5 g of milled powder was uniaxially pressed at a pressure of 5 tons into a specialty designed 2 inch-diameter target holder.

For growing $Cu_2ZnSnSe_4$ thin films, binary chalcogenide powders consisting of CuSe, Cu_2Se, ZnSe and SnSe (each of 99.9 % purity) were mixed at various moles for 24 hours using a plastic container to prepare powder compacted targets. Ten grams of mixed powder were employed throughout experiments. The detailed composition of target is given in table 1.

Table 1. Target composition for growing $Cu_2ZnSnSe_4$ thin films

Target	Powder composition (mole)			
	CuSe	Cu_2Se	ZnSe	SnSe
A	2	-	1	1
B	3	-	1	1
C	4	-	1	1
D	2	0.5	1	1
E	4	0.5	1	1
F	-	1	1	1

The Corning1737 glass substrates were cut into 1 x 5 cm specimens followed by sequential cleaning with ethanol, de-ionized water, and then nitrogen gas drying. The substrate to target distance was kept constant at 50 mm. After initially evacuating the chamber by means of a turbomolecular pump to a base pressure of 10^{-6} Torr , Ar gas (99.9999% purity) was introduced to reach a working pressure of 4.6 x 10^{-2} Torr. 15 minutes pre-sputtering was carried out for the purpose of removing any undesirable contaminants from the targets surface prior to the actual sputtering process. In order to maintain the target composition's stoichiometry and to prevent any damage, the target was regularly replaced every single deposition. All depositions were carried out using 75-125 Watt RF Power at deposition temperatures from room temperature to 200°C.

The phase investigation of the thin films was performed by X-Ray diffraction/XRD (Rigaku DMAX 2500, Japan) using Cu Kα radiation with λ = 1.5405 Å with a diffraction angle, 2θ ranging from 10^0 to 80^0. The determination of the elemental concentration in the bulk films was carried out by means of an Energy Dispersive X-Ray Spectrometer/EDX (EMAX-Horiba, Japan) attached to a Scanning Electron Microscope/SEM (Hitachi S-4100, Japan). The optical transmission spectra were determined by means of a UV-VIS-NIR Spectrophotometer (Cary 500 Varian, USA) with a spectral range of 300-2500 nm. The films electrical preperties were examined by using Van der Paw method at 300 K (ECOPIA HMS-3000, USA).

3. Results and discussion

3.1. $CuInZnSe_2$ thin film preparation

Table 3. Composition of films deposited from targets with various ZnSe content

ZnSe content (wt. %)	Films composition (at. %			
	Cu	In	Zn	Se
0	24.68	25.12	-	50.20
10	19.52	23.78	4.08	52.62
20	20.39	21.95	6.82	50.84
30	21.29	17.22	13.26	48.23
40	18.60	14.11	18.90	48.39

As seen in Table 3, the sputtering target composed of CuSe, InSe and various ZnSe content produce a film with a desired composition . The Zn concentration in the films is found to be proportional with the addition of ZnSe in the sputtering target up to 19.8 at. %.

. The typical X-ray diffraction of films deposited at different Zn atoms concentration is illustrated in the Fig. 1. In comparison with the film without Zn, the CIZSe films have a similar polycrystalline chalcopyrite structure with (112), (220/204) and (312/116) peak orientations. No metallic elements or any secondary phases were detected using XRD which implies all elements were completely reacted to form a single phase chalcopyrite.

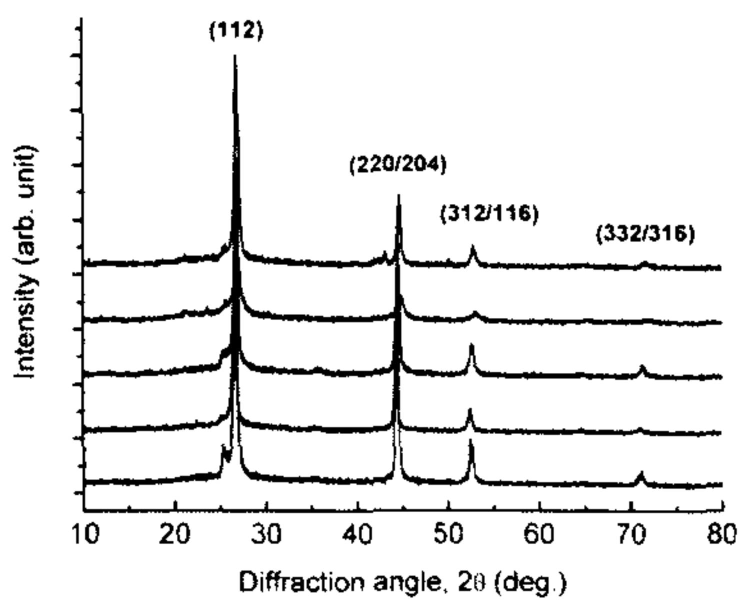
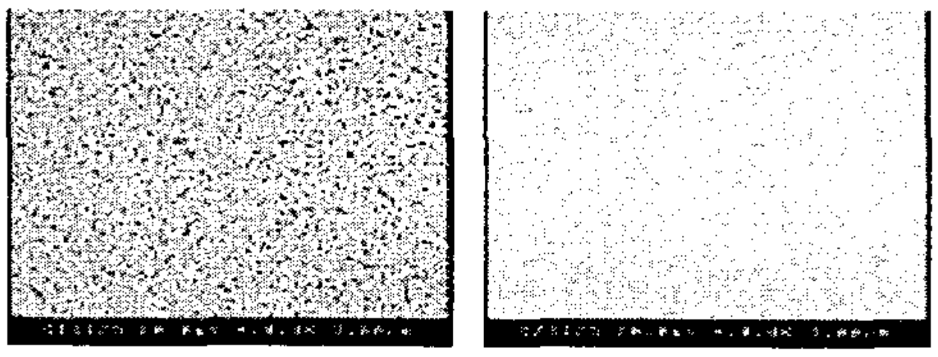


Fig. 1. A typical XRD pattern of films deposited from target with various ZnSe contents

Surface morphology of stoichiometric CuInZnSe$_2$ films are depicted in Fig. 2. Films possess surface with smooth and uniform morphology free of cracks, pin holes, outgrowth or other macroscopic imperfections. On a basis of compositional analysis, such film surface morphology arises from poor Cu and excessive In. The films surface morphology show a texturized surface film as a major consequence of a stoichiometric composition or a higher applied deposition temperature of 200^{0}C.



(a) (b)

Fig. 2. Surfave morphology of films deposited using (a) CuSe-InSe and (b) CuSe-InSe-20 wt. % ZnSe target

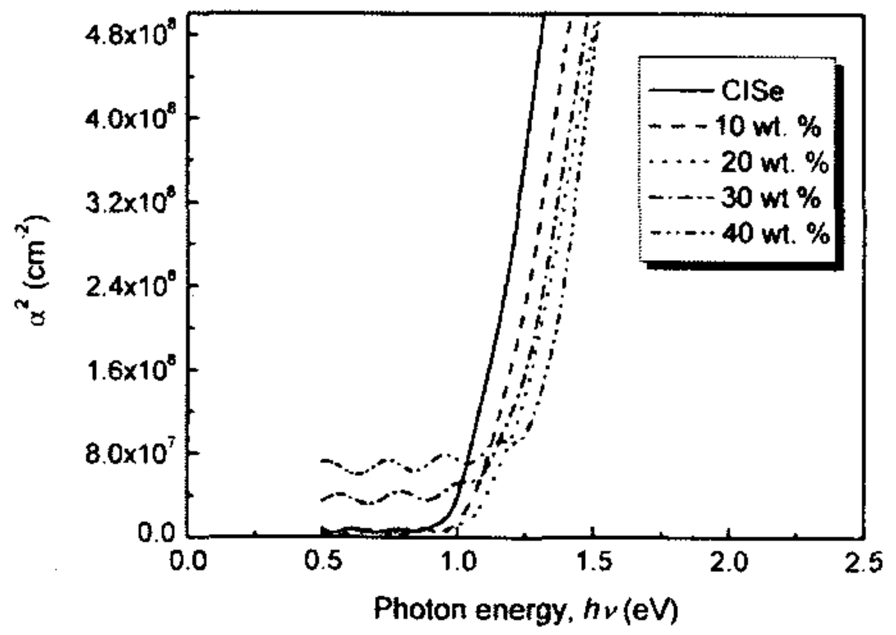


Fig. 3. Optical band gap of films deposited from target with various ZnSe contents fs

The optical characteristics of the CuInZnSe$_2$ films were evaluated. All films possess an absorption coefficient of ~10^4 cm^{-1} above the fundamental band edge. The direct optical band gap of the CISe and CIZSe films is determined by extrapolating the straight line of the square of the absorption coefficient (α^2) to the intercept of the horizontal axis of the photon energy (eV), as depicted in Fig. 3. CISe film demonstrates an optical band gap of 1.0 eV and the optical band gap can be widened by increasing Zn atoms conncentration in the films yielding CIZSe films with a tunable optical band gap between 1.02-1.25 eV.The electrical properties investigation by Hall measurement showed that all films show a p type semiconductor characteristic with hole concentration (n_p) between 10^{12} to 10^{14} cm^{-3}. Hall mobility (μ_H) in the order of 10^1 cm^{2}V^{-1}s^{-1} and resistivity (ρ) of 10^2 Ωcm.

3.2. Cu$_2$ZnSnSe$_4$ thin film preparation

The use of powder target with controlled moles of CuSe, Cu$_2$Se, ZnSe and SnSe powders yielded sputtered films with various compositions as demonstrated in figure 3. It was firstly presumed that the target composed of CuSe, ZnSe and SnSe at 2:1:1 molec omposition (Target A) would be able to deposit a Cu$_2$ZnSnSe$_4$ film with a stoichiometric composition (25at.% Cu,12.5at.% Zn and Sn, 50at.% Se). However, due to the differences of sputtering yield of each element in the target, the film composition was far from the expected composition as seen in figure 4. According to EDX results, the film composition is found to be a function of target mole composition. Near-stoichiometric Cu$_2$ZnSnSe$_4$ film could be successfully deposited using target composed of CuSe:Cu$_2$Se:ZnSe:SnSe at 4:0.5:1:1 moles (Target E).

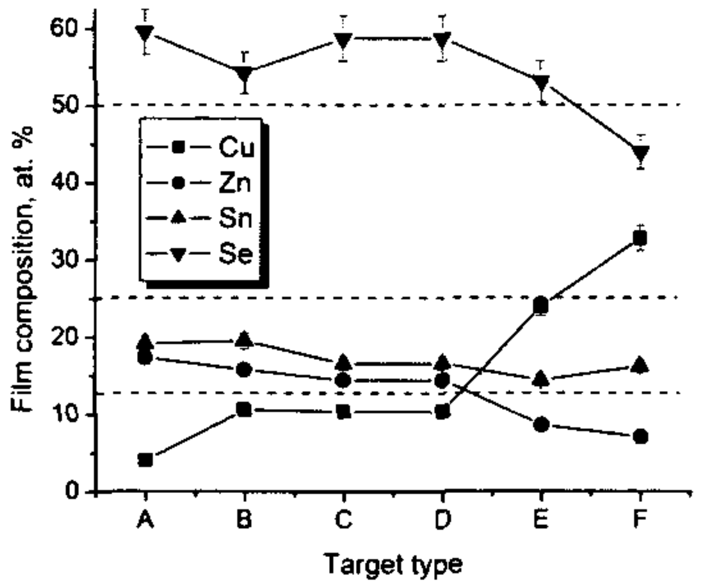


Fig. 4. Film composition as a function of sputtering target type with various moles. Dotted lines represent stoichiometric value for each element.

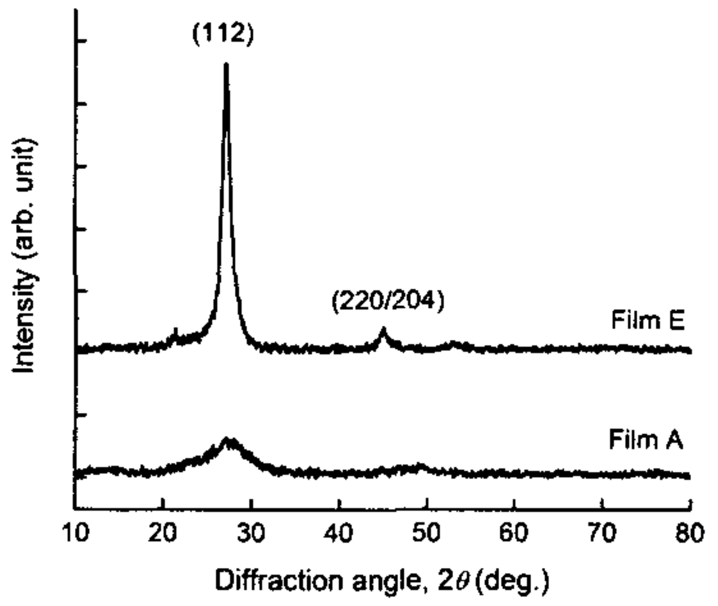


Fig. 5. The typical X-ray diffraction pattern of films A and E deposited from respective sputtering targets.

The X-ray diffraction pattern of films deposited from different target is shown in figure 5. Generally speaking, the films grew as a single phase of Cu$_2$ZnSnSe$_4$ which is known as a stannite phase with a strong (112) reflection. Non-stoichiometric film deposited from Target A (Film A) reveals poor degree of crystallinity whereas films with nearly Cu$_2$ZnSnSe$_4$ stoichiometric composition deposited from Target E (Film E) demonstrated higher degree of crystallinity.

Surface morphology and cross section of $Cu_2ZnSnSe_4$ film are depicted in figure 6. Film consists of irregular texture with various sizes of grain and dense structure without any microcracks or pinholes. Cross sectional analysis also demonstrates the film that grew along the (112) crystallographic plane shows a strong adhesion to the Corning 1737 glass substrates. In this experiment, the thickness of $Cu_2ZnSnSe_4$ was approximately determined as 900-1200 nm. An absorption coefficient of $10^4 cm^{-1}$was calculated from the transmission data. The direct optical band gap of the films was determined by the same method with $CuInZnSe_2$ thin film previously (see figure 7).

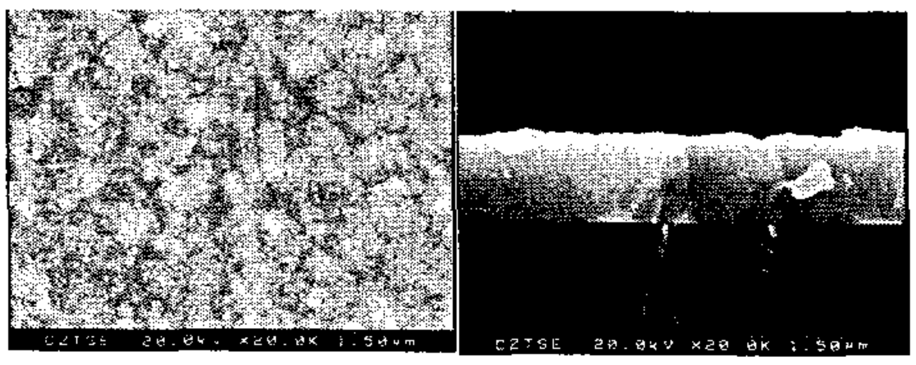


Fig. 6. Plane (left) and cross section (right) of $Cu_2ZnSnSe_4$ film deposited from Target E.

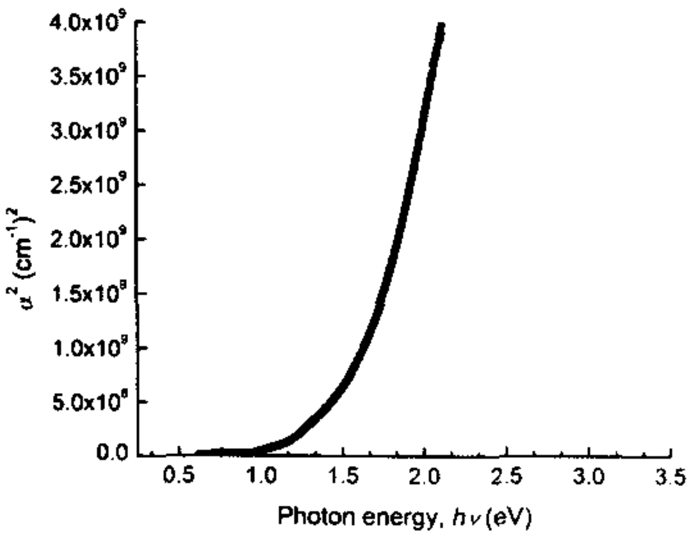


Fig. 7. Plot of a^2vs *hn* of $Cu_2ZnSnSe_4$ thin film

4. Conclusions

$CuInZnSe_2$ and $Cu_2ZnSnSe_4$ thin films were prepared by radio frequency (RF) magnetron sputtering from mixed binary chalcogenide powder targets. $CuInZnSe_2$ thin films show a single phase chalcopyrite crystal structure independent from Zn concentration in the films. $CuInZnSe_2$ films optical band gaps were varied from 1.0 eV to 1.25 eV proportional with an increasing of Zn content to 18.9 at. %.

By controlling CuSe and Cu_2Se mole composition in the targets, near stoichiometric and stannite single phase $Cu_{-2}ZnSnSe_4$ thin films could be successfully deposited. $Cu_2ZnSnSe_4$ thin films show a predominant (112) reflection with a strong adhesion to the substrate. The band gap of film is determined to be 1.5 eV. It is found that control of target compositions is of essential to deposit $CuInZnSe_2$ and $Cu_2ZnSnSe_4$ thin films.

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