[2007-12-PV-008]

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

Kyoo Ho Kim*, Rachmat Adhi Wibowo

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

Kyoo Ho Kim*, Rachmat Adhi Wibowo

Abstract In this paper, we report the research highlight on the preparation and characterization of Indium-free $Cu_2ZnSnSe_4$ and Indium-reduced $CuInZnSe_2$ thin films in order to seek the viability of these absorber materials to be applied in thin film solar cells. The films of $Cu_2ZnSnSe_4$ and $CuInZnSe_2$ were prepared using mixed binary chalcogenides powders. It was observed that Cu concentration was a function of substrate temperature as well as CuSe mole ratio in the target. Under an optimized condition, $Cu_2ZnSnSe_4$ and $CuInZnSe_2$ thin films grew with strong (112), (220/204) and (312/116) reflections. Both $Cu_2ZnSnSe_4$ and $CuInZnSe_2$ films were found to exhibit a high absorption coefficient of 10^4cm^{-1}. $Cu_2ZnSnSe_4$ film showed a band gap of 1.5 eV which closes to the optimum band gap of an ideal solar absorber for a solar cell. On the other side, an increase of optical band gap from 1.0 to 1.25 eV was found to be proportional with an increase of Zn concentration in the $CuInZnSe_2$ film. All films in this study revealed a *p*-type semiconductor characteristic.

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

* Department of Materials Science and Engineering Yeungnam University
■ E-mail : khokim@yu.ac.kr ■ Tel : (053) 810-2475 ■ Fax : (053) 810-4628

1. Introduction

Recently, the availability of indium (In) and gallium (Ga) elements in $Cu(In1_{-x}Ga_x)Se_2$ and $CuInS_2$ compounds is a focus of discussion regarding the high material cost of large-scale production solar cells [1]. Substitution of In in the chalcopyrite $CuInSe_2$ films by inexpensive materials of zinc (Zn) and tin (Sn) is considered as an alternative way to replace the usage of expensive In, yielding a $Cu_2ZnSnSe_4$ quaternary compound. $Cu_2ZnSnSe_4$ is a direct *p*-type semiconductor with an optical band gap of 1.44 eV and an absorption coefficient larger than 10^4cm^{-1} which match with the material prerequisites for a solar absorber material [4,5] This novel quaternary compound can be synthesized by replacing half of the In in the chalcopyrite $CuInSe_2$ with Zn and the other half with Sn. Elsewhere, we

demonstrated the successful preparation of $Cu_2ZnSnSe_4$ films using conventional radio frequency (RF) magnetron sputtering and pulsed laser deposition[6,7].

In addition, the attention to the $AB^{II}C_2^{VI}$-A^IB^{VI} alloy systems (A^I= Cu, Ag, B^{III}= Al, Ga, In, C^{VI}= S, Se, Te; A^{II}= Zn, Cd, Hg, and B^{VI}= S, Se,Te) for Indium-reduced solar cell has also increased in importance since the first report on successful fabrication of $CuInZnSe_2$ thin films by evaporation and selenization [8]. The$(CuInSe_2)_X$-$(2ZnSe)_{1-X}$ solid solution as a part of $A^IB^{II}C_2^{VI}$ - A^IB^{VI} alloy systems 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 above 10^4cm^{-1} [9]. With respect to $CuInSe_2$, it is realized that the presence of Zn in the $(CuInSe_2)_X$-$(2ZnSe)_{1-X}$ system possibly will reduce the material cost by reducing partially the expensive In.

In this paper, a research highlight on the preparation of Indium-free $Cu_2ZnSnSe_4$ and Indium-reduced $CuInZnSe_2$ thin films by means of sputtering technique using binary chalcogenide powder targets is presented and discussed.

2. Experimental details

For preparing $Cu_2ZnSnSe_4$ and $CuInZnSe_2$ thin films, two routes of target preparation were carried out. $Cu_2ZnSnSe_4$ films were prepared using sputtering targets consisting of binary chalcogenide powders of CuSe, Cu_2Se, ZnSe and SnSe (each of 99.9 % purity). The chalcogenide powders were mixed at various moles to prepare powder compacted targets with various compositions. The detailed composition of targets is given in table 1. In order to prepare sputtering targets for growing $CuInZnSe_2$ 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 pre-mixed CuSe and InSe 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 for 24 hours. The 5 g of milled powder was uniaxially pressed at a pressure of 5 tons into a specialty designed 2 inch-diameter target holder.

The Corning 1737 glass substrates were cut into 1 x 5 cm specimens followed by a sequential cleaning as described elsewhere [6,7]. 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. In this experiment, $Cu_2ZnSnSe_4$ films were prepared at 75 W radio frequency (RF) powers whereas $CuInZnSe_2$ films were optimized using 125 W RF powers. Substrate temperature was varied from room temperature to 200℃.

The phase investigation of the thin films was performed by X-Ray diffraction/XRD (Rigaku DMAX 2500, Japan) using Cu Ka radiation with λ =1.5405 Å with a diffraction angle, 2θ ranging from 10^0 to 80^0. The

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

Target ID	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

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). The films electrical properties were examined by using Van der Paw method at 300K (ECOPIA HMS-3000, USA).

3. Results and discussion

3.1. $Cu_2ZnSnSe_4$ thin films preparation

It was firstly presumed that target A could be employed to prepare a film with a $Cu_2ZnSnSe_4$-like stoichiometric composition i.e. 25 at.% Cu, 12.5 at.% Zn and Sn, 50 at.% Se. However, due possibly to the difference of surface binding energy of each elements which Cu (3.503 eV $atom^{-1}$) is the highest amongst Zn (1.352 eV $atom^{-1}$), Sn (3.122 eV $atom^{-1}$) and Se (2.462 eV $atom^{-1}$) [10], the sputtering yield of Cu is the lowest leading to the non-stoichiometric composition of films prepared using target A as can be seen on film in figure 1. An effort to increase Cu concentration in the film was carried out by increasing the amount of Cu source in the target. It was observed that adding CuSe composition in the sputtering target up to 4 moles led to an increase of Cu concentration in the films as represented in the composition of films prepared using target B and C, however, with an insignificant result. Seeing that the need to increase Cu concentration in the film is inevitable for growing a film with a stoichiometric composition, the Cu source in the target was modified with additional 0.5 moles powder as represented in the Target D and E compositions. The composition of films prepared by these targets demonstrates a significant

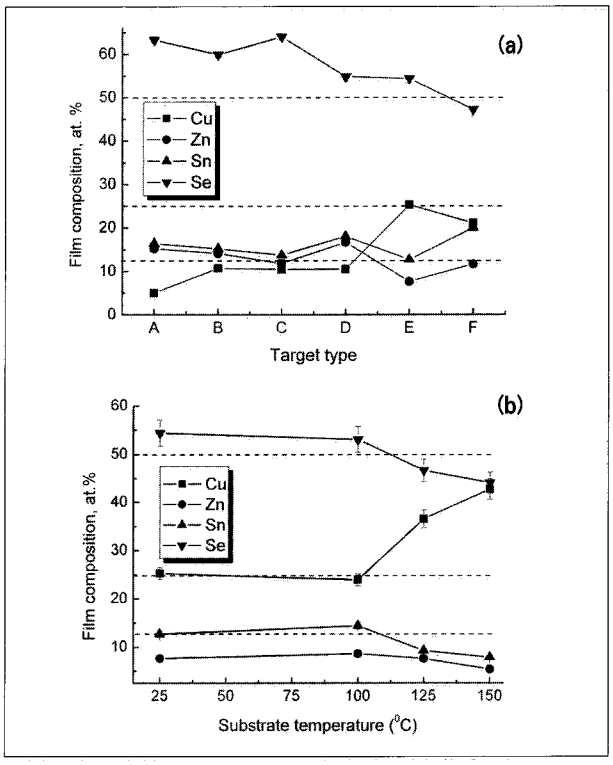


Fig. 1 (a) Composition of film prepared at room temperature as a function of target composition, and (b) composition of film prepared using target E at various substrate temperatures.

increase of Cu concentration in the film close to 25 at.% when using CuSe:Cu_2Se:ZnSe:SnSe = 4:0.5:1:1 target mole composition (Target E). Figure 1b depicts the substrate temperature dependence of composition of film prepared using target E.

The typical X-ray diffraction pattern of films (normalized intensity) prepared using various target compositions (target A to F) at room temperature is represented in figure 2a. The non-stoichiometric film deposited from target A (Film A) reveals a poor degree of crystallinity or tends to have an amorphous state whereas the film with a nearly $Cu_2ZnSnSe_4$ stoichiometric composition deposited from target E (Film E) demonstrates a highly polycrystalline state as observed by the reduce of full-width half-maximum (FWHM). The X-ray diffraction pattern of Film E grown at various substrate temperatures is given in figure 2b.

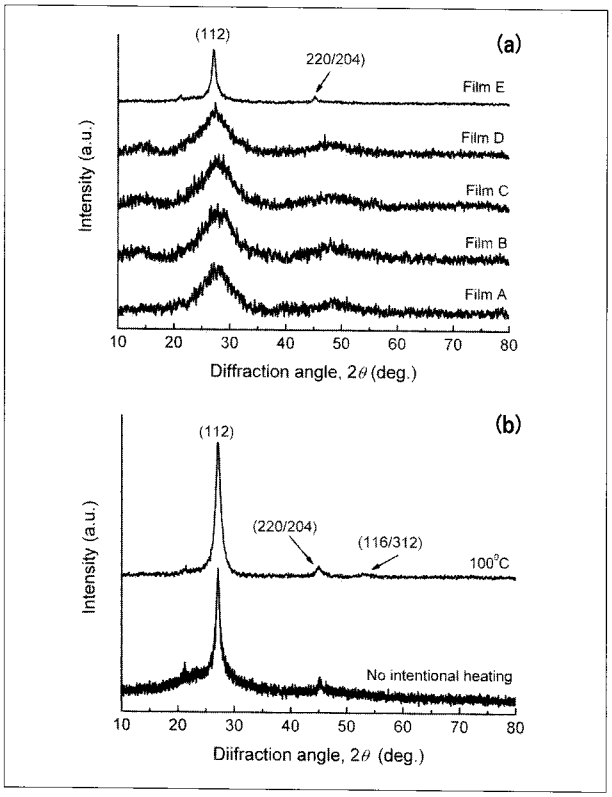


Fig. 2 (a) The typical X-ray diffraction pattern of films deposited from respective sputtering targets at room temperature, (b) X-ray diffraction pattern of film E prepared at various substrate temperatures.

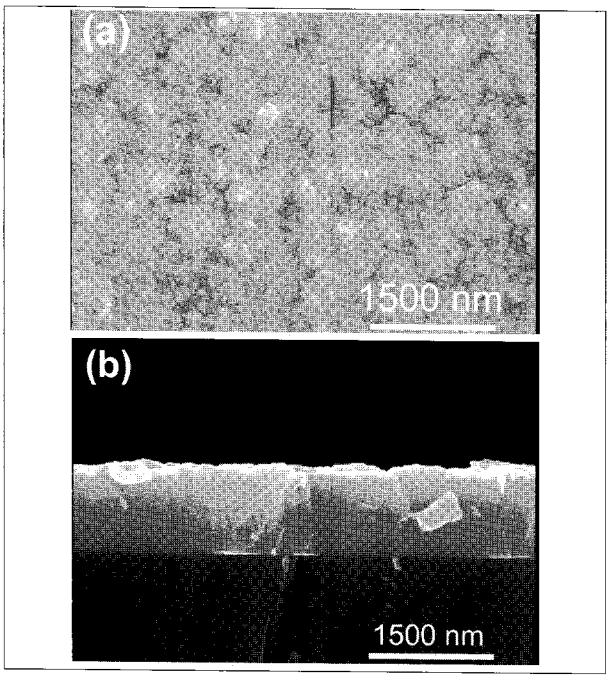


Fig. 3 (a) Plane and (b) cross sectional images of $Cu_2ZnSnSe_4$ film prepared from Target E at 100℃ substrate temperature.

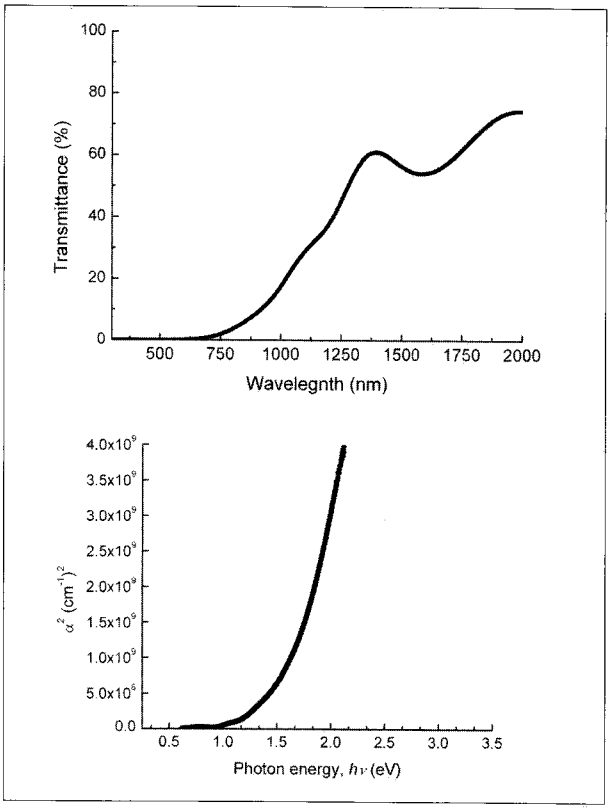


Fig. 4 (a) Optical transmittance of $Cu_2ZnSnSe_4$ film prepared from target E,(b) Plot of a2vs hn of the same film.

The film preparation beyond 100℃ substrate temperature led to a poor film adhesion and film delamination due probably to off-stoichiometry (see figure 1b). It is also shown that as substrate temperature is increased to the optimum substrate temperature of 100℃, the degree of crystallinity of films increase proportionally and a weak reflection of (220/204) is occurred.

On a basis of stannite phase $Cu_2ZnSnSe_4$ compound diffraction pattern [5,6], the Film E grew as a single phase of $Cu_2ZnSnSe_4$ with a predominant (112) reflection at $2\theta \sim 27.04^0$ alongside with a weak (220/204) reflection at $2\theta \sim 44.9^0$. A complete stoichiometric reaction between four elements of Cu, Zn, Sn and Se to form a stoichiometric and single phase of $Cu_2ZnSnSe_4$ compound thin film can possibly be attributed to an

improvement of crystallinity. The calculation of lattice parameters a, c and tetragonal distortion $\eta \equiv c/2a$ of $Cu_2ZnSnSe_4$ film prepared using Target E at 100℃ substrate temperature gives a = 5.6953 Å, c=11.4871 Å and η =1.0085. These results are closer to the results reported by Matsushita et al. [5] than that of by Olekseyuk et al. [4]. Conclusively, the film exhibited a tetragonal deformation, $\eta > 1$, i.e. the film is dilated along the c-axis.

Surface morphology and cross section of $Cu_2ZnSnSe_4$ film prepared using target E are depicted in figure 3a and b. Film consists of irregular texture with various sizes of grain and dense structure. Film was found to have a strong adhesion to the substrate. In this experiment, the thickness of $Cu_2ZnSnSe_4$ was approximately determined to be 1100-1200 nm.

The optical characteristics of the films were evaluated in terms of the optical transmission spectra, absorption coefficient and band gap. Figure 4a shows that the $Cu_2ZnSnSe_4$ film prepared using target E is transparent in the far to infra-red spectrum (1000~2000 nm) with an average transmittance of 60%, while being highly absorbent in the near UV and visible spectra (300~800 nm). The optical band gap (E_g) of the $Cu_2ZnSnSe_4$ film can be determined by the extrapolation method from absorption edge. The absorption edge for direct interband transition is given by $\alpha^2 = h\nu - E_g$, where h is Planck's constant, and ν is the frequency of the incident photon. The coefficient of absorption α is defined as $I = I_0 e^{-\alpha t}$ where I is the intensity of transmitted light I_0 is the intensity of incident light, and t is the thickness of $Cu_2ZnSnSe_4$ film. The transmittance is defined as I/I_0 therefore α can be obtained. Fig. 4b is the plot of α^2 vs $h\nu$. The energy gap can then be obtained from the intercept of α^2 vs hv, yielding a band gap of 1.5 eV, i.e. increases slightly in comparison with the single crystal band gap [6]. The slight film band ga difference of sputtered film from the single crystal value could possibly be originated from the tetragonal distortion η exerts on the sputtered $Cu_2ZnSnSe_4$ film [11]. The Hall measurement revealed that the film prepared from target E exhibit a p-type semiconductor characteristic.

3.2. $CuInZnSe_2$ thin films preparation

Table 2 of film compositional analysis result revealed that at the optimum substrate temperature of 200℃, the sputtering targets composed of CuSe, InSe and various ZnSe contents produce a film with various Zn concentration. The Zn concentration in the film is found to be proportional with the addition of ZnSe in the sputtering target up to 40 wt. %. As also summarized in Table 1, the film without Zn (TF-0 film) showed a $CuInSe_2$-like composition with nearly 25 at.% of metals and 50 at.% Se concentrations. The In concentration can be reduced almost 44 % from the 25.12 at.% to 14.11 at. % due to the fact of the gradual increase of Zn concentration as can be seen in Table 3. The apparently Cu and In reduction in the film as the Zn concentration increases is due to an antisite substitution of Zn on the Cu and In sites in chalcopyrite $CuInSe_2$ structure [12].

In order to confirm the structure of films prepared at 200℃ substrate, X-ray diffraction patterns of films were taken as depicted in figure 5. A diffraction pattern corresponding to a chalcopyrite structure with (112), (220/204) and (312/116) peak orientations is predominantly observed in the case of the TF-0 film, which therefore confirms that it is a polycrystalline $CuInSe_2$ film. The fact that the (112) reflection is the strongest indicates that the $CuInSe_2$ thin film is oriented along the (112) plane parallel to the substrate. However, the TF-0 film exhibits a low intensity peak corresponding to the In_2Se_3 phase, which most probably occurs due to the excessive In. The films with various Zn concentrations (TF-10 to TF-40) demonstrate diffraction patterns corresponding to a chalcopyrite structure as well. As seen in figure 5, the films exhibit similar (112), (220/204), and (312/116) reflections, thus

Table 2. Composition of films deposited from targets with various ZnSe content.

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

Table 3. Percent indium reduction and compound designation of $CuInZnSe_2$ films.

Film ID	Films composition (at. %)	
	In reduction (%)	Compound designation
TF-0	0	$CuInSe_2$
TF-10	5.3	$Cu_{0.82}InZn_{0}.18Se_2$
TF-20	12.61	$Cu_{0.83}In_{0.89}Zn0.28Se_2$
TF-30	31.45	$Cu_{0.82}In_{0.67}Zn0.51Se_2$
TF-40	43.83	$Cu_{0.72}In_{0.55}Zn0.73Se_2$

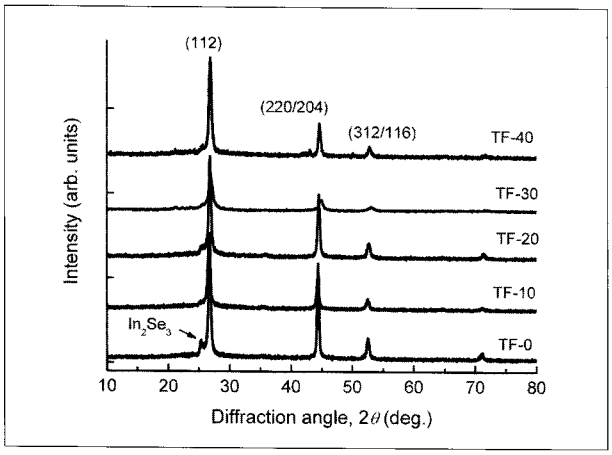


Fig. 5 A typical XRD pattern of chalcopyrite $CuInZnSe_2$ films prepared using target with various ZnSe contents at 200°substrate temperature.

confirming that they are polycrystalline $CuInZnSe_2$ films with the designated compounds mentioned in table 3. All of the films are observed to be polycrystalline in nature without any sharp differences in their diffraction patterns being observed as the Zn is increased to 18.9 at. %. Taking into account the maximum Zn concentration in the films, the $CuInZnSe_2$ films in this experiment exhibit no apparent chalcopyrite-sphalerite phase transition according to the $(CuInSe_2)_X(2ZnSe)_{1-X}$

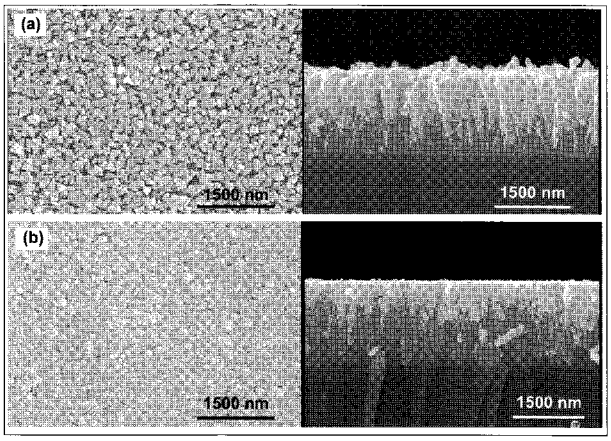


Fig. 6 Surface morphological and cross sectional images of film (a) TF-0 and (b) TF-20.

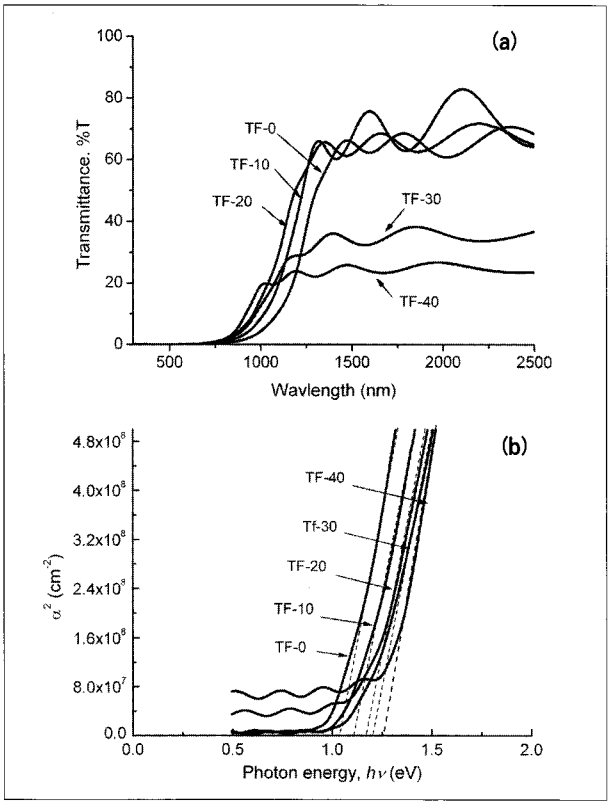


Fig. 7 (a) Optical transmittance and (b) band gap of $CuInZnSe_2$ films.

solid solution crystallographic data [13].

Surface morphology and cross sectional images of TF-0 ($CuInSe_2$) and TF-20 ($Cu_{0.83}In_{0.89}Zn_{0.28}Se_2$) films are depicted in Fig. 6a and 6b. Films possess surface

with smooth and uniform morphology free of cracks, pin holes, outgrowth or other macroscopic imperfections. In this experiment, it is found that an increase of Zn concentration in the films is followed by the decrease of film grain size probably due to the role of zinc as an additional nucleation site that enhances nucleation thus increases the number of grain boundary.

Figure 7a shows that the optical transmission characteristic of $CuInZnSe_2$ films deposited on Corning 1737 glass under identical deposition conditions. The films are transparent from infra red to the end of visible spectrum with an average transmittance of 70%, while being highly absorbent in the short wavelength of visible spectra. The film optical transmittance edge can gradually be shifted towards a shorter spectrum wavelength by proportional increase of zinc concentration. This result demonstrate the same optical transmission tendency as $Cu(In,Al)Se_2$ thin films when the aluminum concentration is increased from 0 to 0.59 mole fractions in order to reduce indium as well as to increase the band gap [14]. Band gap of the $CuInZnSe_2$ films was determined by the same procedure as determining $Cu_2ZnSnSe_4$ band gap, and the results are depicted in figure 7b.

TF-0 ($CuInSe_2$) film demonstrates an optical band gap of 1.0 eV and the optical band gap of film can be increased with the increasing Zn concentration in the film, yielding film with engineered optical band gaps ranging from 1.0 to 1.25 eV (TF-0 toTF-40). It is seemed that the presence of Zn in the $CuInZnSe_2$ thin film altered the cation-anion bond length which increases the band gap of film[11].The smaller ionic radius of the Zn than the In in the tetrahedrally coordinated chalcopyrite structure can be considered as the origin of the bond length alteration. The electrical properties investigation by Hall measurement showed that all films showed a *p* type semiconductor characteristic.

4. Conclusion

$Cu_2ZnSnSe_4$ and $CuInZnSe_2$ thin films were successfully prepared by radio frequency (RF) magnetron sputtering from mixed binary chalcogenide powder targets for Indium-free and Indium-reduced thin film solar cell application. By controlling CuSe and Cu_2Se mole composition in the target, near stoichiometric and stannite single phase $Cu_2ZnSnSe_4$ thin films could be successfully deposited using single target. $Cu_2ZnSnSe_4$ 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. $CuInZnSe_2$ thin films show a single phase chalcopyrite crystal structure independent from Zn concentration in the films. The composition of In in the film could significantly be reduced to approximately 45 % by increasing Zn. $CuInZnSe_2$ film optical band gap was varied from 1.0 eV to 1.25 eV proportional with an increasing of Zn content. It was found that control of target compositions is of essential to prepared $CuInZnSe_2$ and $Cu_2ZnSnSe_4$ thin films. These preliminary results also revealed that the properties of sputtered $Cu_2ZnSnSe_4$ and $CuInZnSe_2$ thin films match with the solar absorber material prerequisites and could potentially be applied as an indium-free and indium-reduced thin film solar cell with an advantage of having an engineered band gap.

Acknowledgement

This work was supported by Korean Ministry of Commerce, Industry and Energy (MOCIE) under New & Renewable Energy R&D Program, subcontract No. 2005-N-PV12-P-03.

References

[1] B.A. Andersson, "Materials availability for large scale thin film photovoltaics", Prog. Photovolt. Res. Appl. 8 (2000) 61-76.

[2] S. Marsillac, P.D. Paulson, M.W. Haimbodi, R.W. Birkmire, W.N. Shafarman, "High efficiency solar cells based on Cu(InAl)Se_2 thin films". Appl. Phys. Lett. 81 (2002) pp. 1350-1352.

[3] H. Katagiri, "Cu_2ZnSnS_4thin film solar cells", Thin Solid Films 480-481 (2005) pp. 426-432.

[4] I.D. Olekseyuk, L.D. Gulay, I.V. Dydchak, L.V. Piskatch, O.V. Parasyuk, O.V. Marchuk, "Single crystal preparation and crystal structure of the $Cu_2Zn/Cd,Hg/SnSe_4$ compounds", J. Alloy. Compds. 340 (2002) pp. 141-145.

[5] H. Matsushita, T. Maeda, A. Katsui, T. Takazawa, "Thermal analysis and synthesis from the melts of Cu-based quaternary compounds Cu-III-IV-VI_4 and Cu_2-II-IV-VI_4 (II=Zn, Cd; III=Ga, In, IV=Ge, Sn; VI=Se)", J. Cryst. Growth 208 (2000) pp. 416-422.

[6] R.A. Wibowo, W.S. Kim, E.S. Lee, B. Munir, K.H. Kim, "Single step preparation of quaternary $Cu_2ZnSnSe_4$ thin films by RF magnetron sputtering from binary chalcogenide targets", J. Phys. Chem. Solids 68 (2007) pp. 1908-1913.

[7] R.A. Wibowo, E.S. Lee, B. Munir, K.H. Kim, "Pulsed laser deposition of $Cu_2ZnSnSe_4$ thin films", Phys. Stat. Sol. (a) 204 (2007) pp. 3373-3379.

[8]. V. F. Gremenok, E. P. Zaretskaya, V. M. Siarheyeva, K. Bente, W. Schmitz, V. B. Zalesski, H. J. Moller, "Investigation of $CuInZnSe_2$ thin films for solar cell applications", Thin Solid Films 487 (2005) pp. 193-198.

[9]. I. V. Bodnar, V. F. Gremenik, W. Schmitz, K. Bente, Th. Doering, "Preparation and investigation of $(CuInSe_2)_X$-$2(ZnSe)_{1-X}$ and $(CuInTe_2)_X$-$2(ZnTe)_{1-X}$ solid solution crystals", Cryst. Res. Technol. 39 (2004) pp. 301-307.

[10] M.P. Seah, C.A. Clifford, F.M. Green, I.S. Gilmore, "An accurate semi-empiricxal equation for sputtering yields I: for argon ions", Surf. Interface Anal. 37 (2005) pp. 444-458.

[11] J.E. Jaffe, A. Zunger, "Theory of the band gap anomaly in ABC_2 chalcopyrite semiconductors", Phys. Rev. B 29 (1984) pp. 1882-1906.

[12] S. Schorr, M. Tovar, D. Sheptyakov, L. Keller, G. Geandier, "Crystal structure and cation distribution in the solid solution series 2(ZnX)-$CuInX_2$ (X=S, Se, Te)", J. of Phys. and Chem. of Solids 66 (2005) pp. 1961-1965.

[13] I.V. Bodnar, V. F. Gremenok, W.Scmitz, K.Bente,Th.Doering,"Preparationandin-vestigationof $(CuInSe_2)_X(2ZnSe)_{1-X}$ and $(CuInTe_2)_X(2ZnTe)_{1-X}$ solid solution crystals", Crys. Res. Rechnol. 39 (2004) pp. 301-307.

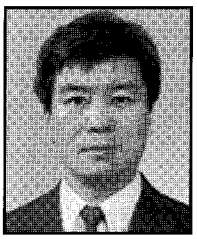
[14] P.D Paulson, M.W. Hambodi, S. Marsillac, R.W. Birkmire, W.N. Shafarman, "$Cu(In_{1-X}Al_X)Se_2$ Se_2 thin films and solar cells", J. Appl. Phys. 91 (2002) pp. 10153-10156.

Rachmat Adhi Wibowo

2002 B.Eng. Department of Metallurgy, University of Indonesia
2005 M.S. Department of Materials Science and Engineering, Yeungnam University

Current position : PhD student since 2005, Department of Materials Science and Engineering, Yeungnam University
(E-mail : wibowo@ynu.ac.kr)

Kyoo Ho Kim



1974년 B.S. Kyungpook National University
1977년 M.S. Kyongpook National University
1987년 Dr. Eng. Tokyo University

Current position : Professor at Department of Materials Science and Engineering, Yeungnam university
(E-mail : khokim@yu.ac.kr)