

Sputtering Deposition of CuInSe_2 and CuInZnSe_2 Thin Films using Mixture Binary Chalcogenide Powders

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

Abstract : In this study, CuInSe_2 (CISE) and CuInZnSe_2 (CIZSe) thin films were prepared on Corning 1737 glass by radio frequency (RF) magnetron sputtering from binary chalcogenide mixed powder targets. The targets were initially prepared by mixing appropriate weights of CuSe, InSe powder and various ZnSe contents. From the film bulk analysis result, it is observed that Zn concentration in the films increases proportionally with the addition of ZnSe in the sputtering targets. Under optimized conditions, CISE and CIZSe thin films grow as a chalcopyrite structure with strong (112), (220/204) and (312/116) reflections. Films are found to exhibit a high absorption coefficient of 10^4 cm^{-1} . An increasing of optical band gap from 1.0 eV (CISE) to 1.25 eV (CIZSe) is found to be proportional with an increasing of Zn concentration as expected. All films have a p-type semiconductor characteristic with a carrier concentration in the order of 10^{14} cm^{-3} , a mobility about $10^1 \text{ cm}^2 \cdot \text{s}^{-1}$ and a resistivity at the range of 10^2 - $10^6 \text{ W} \cdot \text{m}$.

1. Introduction

The first report on the chalcopyrite CuInSe_2 (CISE) thin film solar cell [1] and the subsequent investigations on its optimization [2-3] have spurred efforts to study chalcopyrite CISE compound physical properties [4]. To date, the CISE-based material with an additional gallium ($\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ /CIGSe) is considered to be one of promising materials for the thin film solar cell with cell and module efficiency toward 20% and 14% [5,6]. These findings have led many researchers to the extensive studies on ternary $A^I-B^{III}-C_2^{VI}$ ($A = \text{Cu, Ag, B} = \text{Al, Ga, In, C} = \text{S, Se, Te}$) compounds with continuously growing interest in order to investigate their obvious technological potentials, in particular for photovoltaic application. The $A^I-B^{II}-C_2^{VI}$ ternary compounds are known to be isoelectronics analogs of the $A^{II}-B^{VI}$ ($A = \text{Zn, Cd, Hg, B} = \text{S, Se, Te}$) binary compounds and have been investigated to be applied in the wide variety of optoelectronics devices, light-emitting diodes and solar cells [7].

Recently, attention to the $A^I-B^{II}-C_2^{VI} - A^{II}-B^{VI}$ systems for solar cell application has grown noticeably since the first report on successful fabrication of CuInZnSe_2 (CIZSe) thin films by evaporation-selenization technique and their I - V characteristics [8]. Several following

studies have been devoted to investigate physical characteristics of these systems[9-11]. The $(\text{CuInSe}_2)_x-(2\text{ZnSe})_{1-x}$ 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 [10,11]. With respect to CISE, it is realized that the presence of zinc (Zn) in the $(\text{CuInSe}_2)_x-(2\text{ZnSe})_{1-x}$ 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.

Given that the growth methods are of essential to fit a practical production as well as to prepare device quality thin films, in this paper, an alternative approach for growing CISE and CIZSe thin films by means of sputtering technique using binary chalcogenide powder targets is presented. The structure, electrical as well as optical properties of these films are

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discussed as well.

2. Experimental details

In order to prepare a sputtering target for growing stoichiometric CISE 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 CIZSe 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.

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 4.6×10^{-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 K α radiation with $\lambda = 1.5405 \text{ \AA}$ with a diffraction angle, 2θ , ranging from 10° to 80° . 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 properties were examined by using Van der Paw method at 300 K (ECOPIA HMS-3000, USA).

3. Results and discussion

In order to obtain a film with a stoichiometric composition, a moderate RF power of 75 W was arbitrarily chosen at first to deposit the films. Table 1 shows the composition of films deposited at various deposition temperatures. In accordance with the EDX compositional analysis, at room temperature deposition,

the film composition is found to be far from a predicted composition as demonstrated by a poor Cu and an excessive In. As a deposition temperature is gradually raised to 200°C, the film composition tends to modify toward a stoichiometric CISE film composition which is shown by an increasing of Cu content and a decreasing of In content yielding ultimately a film with a stoichiometric composition of 24.68 at. % Cu, 25.12 at. % In and 50.2 at. % Se.

Table 1. Composition of films deposited at various deposition temperature using mixed CuSe-InSe target

Deposition temp. (°C)	Films composition (at. %)		
	Cu	In	Se
RT	9.96	29.71	60.33
125	16.33	28.39	55.27
150	17.03	28.94	54.03
175	17.3	29.26	53.44
200	23.35	25.77	50.88

Table 2. Composition of films deposited at various deposition temperature using mixed CuSe-InSe-20 wt.% ZnSe target

Deposition Temp. (°C)	Films composition (at. %)			
	Cu	In	Zn	Se
RT	6.55	29.7	3.41	60.32
125	12.15	23.84	9.93	54.08
150	17.4	22.22	8.36	52.02
175	18.56	22.39	6.2	52.85
200	19.36	23.1	6.5	51.04

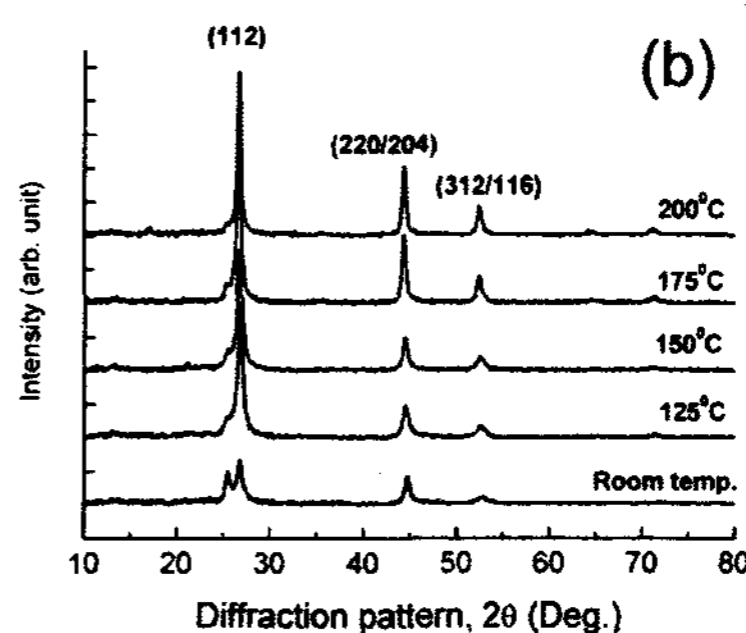
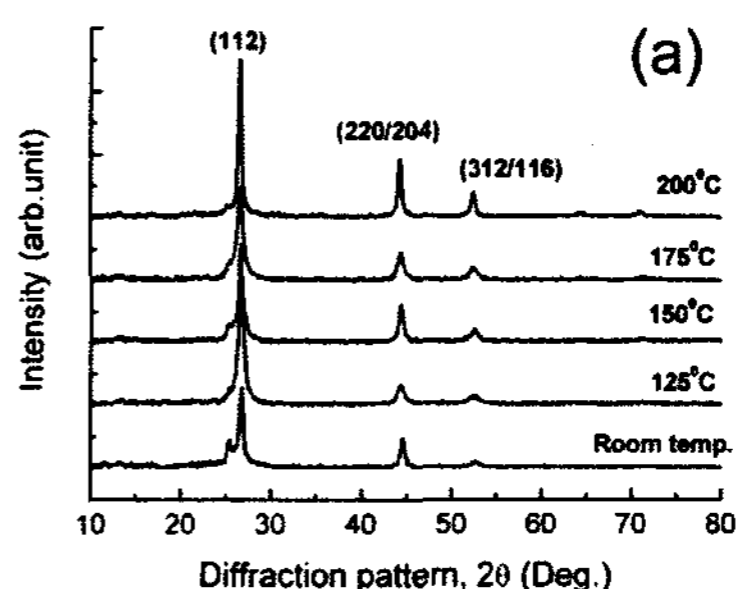


Fig. 1. Typical XRD pattern of films deposited using
(a) mixed CuSe-InSe and
(b) CuSe-InSe-20 wt. %ZnSe target

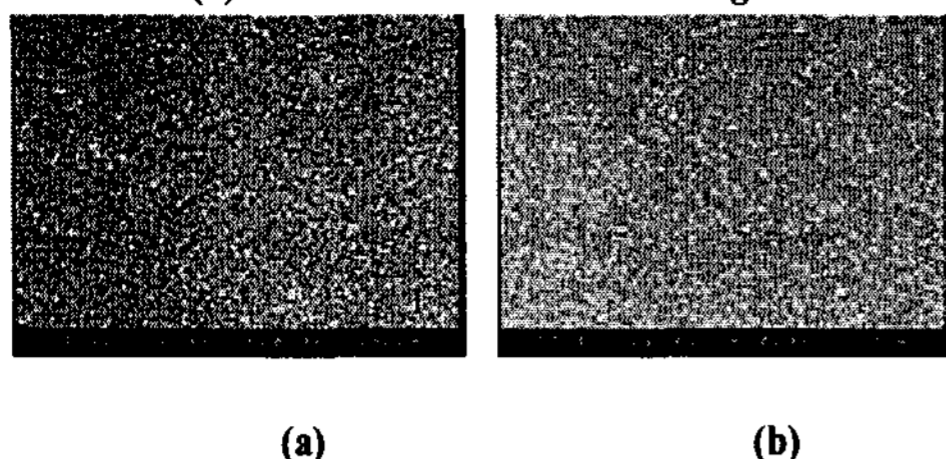


Fig. 2. Surface morphology of films deposited using
(a) CuSe-InSe and (b) CuSe-InSe-20 wt. % ZnSe target

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

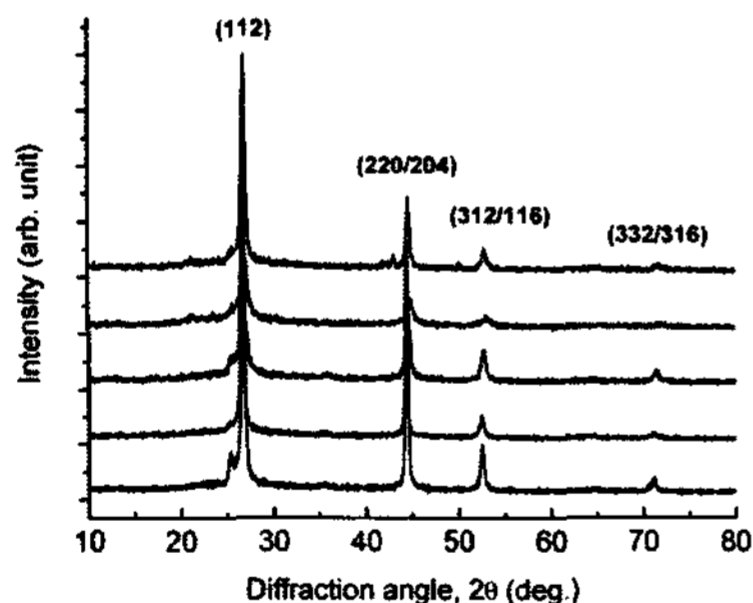


Fig. 3. A typical XRD pattern of films deposited from target with various ZnSe contents

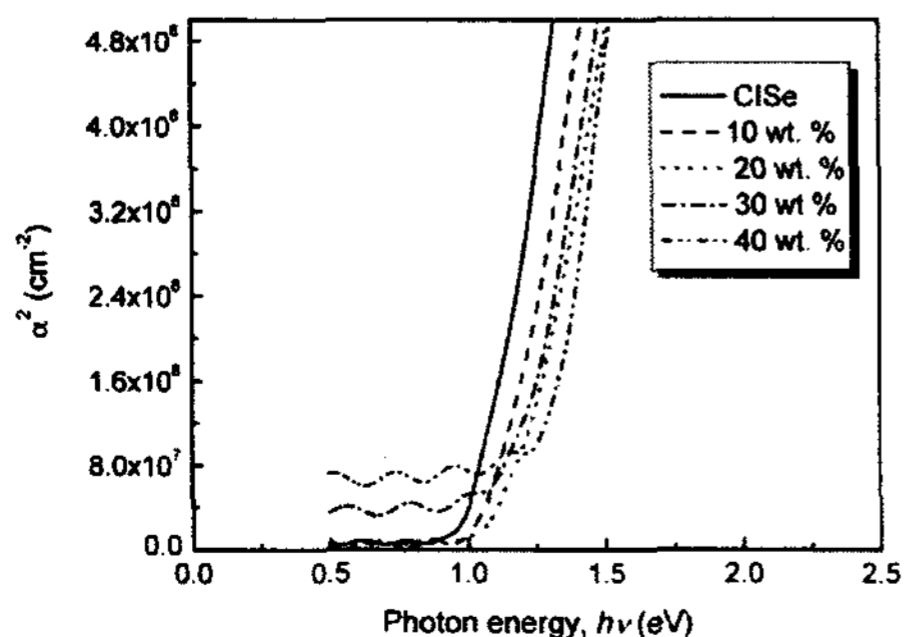


Fig. 4. Optical band gap of films deposited from target with various ZnSe contents fs

As seen in Table 2, the sputtering target composed of CuSe, InSe and 20 wt. % ZnSe does not produce a film with a desired composition after deposited at room temperature as represented by a poor Cu content while exhibits a high content of Zn. As deposition temperature increases to 200°C, the film composition is modified toward an optimum film composition with 19.36 at. % Cu, 23.1 at. % In, 6.5 at. % Zn and 51.04 at. % Se. Reduction of Cu and In content from a stoichiometric CuInSe₂ composition is due to the random substitution of Cu and In sites by Zn atoms [7]. It can be inferred that deposition temperature is of critical to control the films composition. Films deposited at 200°C with various RF power are observed to maintain their stoichiometric composition as well which confirms a film composition optimization independent with any applied RF powers for obtaining a stoichiometric film (data not shown).

Structural phase and degree of crystallinity of films deposited from a sputtering target composed of CuSe and InSe powder at various deposition temperatures under an optimized RF power of 75 W are demonstrated in Fig. 1.a. All films are observed to be polycrystalline in nature with a predominant chalcopyrite structure. However, film deposited at room temperature shows a secondary phase of InSe along with a chalcopyrite phase as reflected by (112), (220/204) and (312/116) peaks orientation. The secondary phase of InSe is thought as a consequence of the film non-stoichiometric composition with poor Cu and excessive In. Fig. 1.b. depicts the structure and degree of crystallinity of films deposited from a sputtering target of mixed CuSe, InSe and 20 wt. ZnSe powder at various deposition temperatures. In general, all films grow and crystallize as a polycrystalline chalcopyrite structure, however, along with a secondary phase of InSe found on the film having poor Cu when it deposited at room temperature. The secondary phase is completely disappeared and left a single chalcopyrite phase of CIZSe film as the film composition modifies to an optimum composition at an elevated deposition temperature of 200°C.

Surface morphology of stoichiometric CISE and CIZSe films deposited at 200°C with RF power of 125 Watt are depicted in Fig. 2. At room temperature, films with non stoichiometric composition 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. CISE and CIZSe films surface morphology show a texturized surface film as a major consequence of a stoichiometric composition or a higher applied deposition temperature of 200°C.

In order to investigate the effects of Zn content in CIZSe films properties, different sputtering targets with various ZnSe contents were prepared. Table 3

summarizes the films composition as a function of ZnSe content in the sputtering target. The Zn atoms concentration in the films is found to be proportional to the ZnSe content in the sputtering target. An additional ZnSe content in the sputtering target lead to an increasing of Zn concentration in the films up to 18.9 at. % while the reduction of Cu as well as In is due to the random substitution of Cu and In sites by Zn atoms.

The typical X-ray diffraction of films deposited at different Zn atoms concentration is illustrated in the Fig. 3. In comparison with CISE film, 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.

The optical characteristics of the films were evaluated. All films possess an absorption coefficient of $\sim 10^4 \text{ cm}^{-1}$ 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. 4. CISE film demonstrates an optical band gap of 1.0 eV and the optical band gap can be widened by increasing Zn atoms concentration 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 $10^1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and resistivity (ρ) of $10^2 \text{ } \Omega \text{ cm}$.

4. Conclusions

CuInSe₂ (CISE) and CuInZnSe₂(CIZSe) thin films were prepared by radio frequency (RF) magnetron sputtering from mixed binary chalcogenide CuSe-InSe-ZnSe powder targets. CISE and CIZSe thin films show a single phase chalcopyrite crystal structure independent from Zn concentration in the films. Films optical band gaps were varied from 1.0 eV (CISE) to 1.25 eV (CIZSe) proportional with an increasing of Zn content to 18.9 at. %. All films show a *p* type semiconductor characteristic with n_p between 10^{12} to 10^{14} cm^{-3} , μ_H in the order of $10^1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and minimum ρ of $10^2 \text{ } \Omega \text{ cm}$.

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.

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