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$Cu_2ZnSnSe_4$ Thin Films Preparation by Pulsed Laser Deposition Using Powder Compacted Target

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Abstract

$Cu_2ZnSnSe_4$ thin films for solar absorber application were prepared by pulsed laser deposition of a synthesized $Cu_2ZnSnSe_4$ compound target. The film's composition revealed that the deposited films possess an identical composition with the target material. Further film compositional control toward a stoichiometric composition was performed by optimizing substrate temperature, deposition time and target rotational speed. At the optimum condition, X-ray diffraction patterns of films showed that the films demonstrated polycrystalline stannite single phase with a high degree of (112) preferred orientation. The absorption coefficient of $Cu_2ZnSnSe_4$ thin films were above 10^4 cm^{-1} with a band gap of 1.45 eV. At an optimum condition, films were identified as a p type semiconductor characteristic with a resistivity as low as 10^{-1} Ωcm and a carrier concentration in the order of 10^{17} cm^{-3}.

Keywords: $Cu_2ZnSnSe_4$, Pulsed laser deposition, Stannite, Single phase, Solar absorber, Optical properties

1. Introduction

It is well known that $Cu(In,Ga)Se_2$ is regarded as one of the most prominent compound materials for a thin film solar cell application. This compound is a chalcopyrite-type semiconductor material which is based on a $CuInSe_2$ structure. Alloying Ga in $CuInSe_2$ is normally incorporated with the purpose of increasing the solar absorber band gap from 1.1 eV to 1.7 eV leading to an increase of open circuit voltage (V_{OC}) of thin film solar cell[1]. The problem at hand, however, it is realized this absorber material contains expensive materials such as Indium (In) and Gallium (Ga), which may hinder its economical competitiveness in offering a low cost solar cell.

Several efforts have been performed either to reduce or to substitute Indium (In) with inexpensive elements, for instances, using Aluminum (Al) instead of Gallium (Ga) as in Chalcopyrite $Cu(In,Al)Se_2$ solar cell, replacing Indium (In) by Zinc (Zn) and Tin (Sn) as in Kesterite Cu_2ZnSnS_4 solar cell for solar absorber layer[2-5]. These solar cells demonstrated promising cell efficiencies with their band gap close to the solar cell band gap requirement value.

Recently, Cu-based chalcopyrite quaternary compounds have been received a considerable attention as a promising materials for low-cost thin film solar cells owing to the suitable band gap energy of 0.96~1.6 eV and to the large absorption coefficient up to 10^4 cm^{-1}.[6,7] Moreover, the absence of the expensive element of In or Ga in these compound has considerably been attracted an attention in order to prepare In-free solar absorber material as an alternative to $CuInSe_2$ and $Cu(In,Ga)Se_2$. $Cu_2ZnSnSe_4$ compound is one of this class of materials which can be synthesize by replacing half of In in Chalcopyrite $CuInSe_2$ with Zinc (Zn) and by replacing the other half with Tin (Sn). $Cu_2ZnSnSe_4$ thin films have been reported to be able to prepared using evaporation, sputtering and pulsed laser deposition (PLD) methods[8-10]. A monograin $Cu_2ZnSnSe_4$ solar cell have been successfully fabricated with an efficiency of 2.16%, therefore opens a wide opportunity to investigate $Cu_2ZnSnSe_4$ technological potential as a thin film solar cell[11]. In this study, we demonstrate the effects of various PLD experimental conditions in order to control the pulsed

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laser deposited $Cu_2ZnSnSe_4$ thin films composition at relatively low substrate temperature regime. Despite a PLD may be a high cost method for preparing large area thin film solar cell yet, its versatility for preparing complex multinary compounds thin films having an identical composition with the target is very attractive[12].

2. Experiment

The Stannite-type $Cu_2ZnSnSe_4$ target was initially prepared by mixing appropriate weights of Cu_2Se, ZnSe, Sn and Se powders (3N purity each) to achieve a composition of a stoichiometric $Cu_2ZnSnSe_4$. These powders were initially ball-milled in ethanol and dried in vacuum evaporator at 80°C. The dried powders were then uniaxially pressed into a mold and cold-isostatic pressed at 250 MPa followed by sintering at 530°C for 6 hours under 2 sccm Ar gas flow. The sintered material was grounded for phase and compositional analysis. The grounded powder composition is of 26.86 at.% Cu, 13.92 at.% Zn, 12.65 at.% Sn and 46.53 at.% Se. X-ray diffraction pattern of the synthesized powder exhibits a single phase of stannite.

A disk-shaped PLD target with a 10 mm diameter was prepared by cold-isostatic pressing the synthesized powder at 250 MPa. The Corning 1737 glass substrates were sliced into 25×25 mm specimens and were ultrasonically cleaned in acetone, ethanol and distilled water before dried in a nitrogen gas stream. The substrate-target distance was 50 mm. After initially evacuating the deposition chamber down to a base pressure of 1.6×10^{-4} Pa, the target was ablated by a pulsed Nd:YAG laser ($\lambda = 1064$ nm, pulse duration of 25 ns, pulsed energy of 300 mJ, repetition rate of 10 Hz) with the calculated laser fluence density was 1.5 J/cm². In this experiment, target rotational speed, substrate temperatures and deposition time were

varied. For measurement, samples were cut from the center of specimen with a size of 10×10 mm.

The phase of the films were examined by X-Ray diffraction using Cu Kα radiation with $\lambda = 1.5405$ Å (Rigaku DMAX 2500, Japan). The film surface and cross section were observed using scanning electron microscopy/SEM (Hitachi S-4100, Japan) equipped with an energy dispersive X-ray/EDX (Horiba, Japan). The optical transmission spectra were recorded using a UV-Vis-NIR spectrophotometer (Cary 500 Varian, USA) with a spectral range of 300~2500 nm. The films resistivity and carrier concentration were examined by using Van der Paw method at 300 K (ECOPIA HMS-3000, USA).

3. Results and Discussion

3.1 Compositions

The experiments were initially began by fixing target rotation at a low speed (5 rotation per minute/ rpm) while deposition time and substrate temperature were varied. Table 1 summarizes the films composition at various deposition conditions. It is clearly revealed that a film deposited at 30 min deposition time at no intentional substrate heating exhibits a composition which is very close with the target material. This result deduces a versatility of PLD for depositing a film having a composition identical with the target material. However, taking into account a stoichiometric composition of $Cu_2ZnSnSe_4$ compound, the film composition is in excessive Cu and Se deficiency situations. The apparently low Se concentration in the films is in reality due to an excessive Cu, whereas Zn and Sn maintain their total composition roughly 24 at.%. This is understandable regarding the Zn and Sn role as a replacement of In in the Chalcopyrite $CuInSe_2$, a sum of their atomic compositions has one-fourth of overall compound atomic composition. In order to optimize film composition toward a stoichiometric composition

Table 1. Film composition as a function of PLD experimental conditions

Deposition time (min.)	Substrate temp. (°C)	Thickness (nm)	Rotation (rpm)	Film composition (at.%)			
				Cu	Zn	Sn	Se
30	No heating	340	5	27.49	13.39	10.14	48.99
30	200	340	5	27.09	13.13	13.31	46.48
30	250	340	5	27.09	13.10	12.19	47.63
60	200	630	5	24.75	11.08	14.32	49.84
90	200	900	5	22.60	9.91	15.09	52.40
60	200	630	10	21.92	9.99	13.50	54.59
60	200	630	15	21.87	9.03	14.16	54.93

of $Cu_2ZnSnSe_4$ compound, control of the film composition was performed by increasing deposition time to 90 min at various substrate temperatures. Cu concentration tends to decrease with an increase of deposition time from 30 to 90 min which is also followed by an increase of Se concentration. This stage led to a nearly stoichiometric composition of film deposited at $200^{\circ}C$ substrate temperature and 60 min deposition time. Various target rotations were further intentionally applied to search for an improvement of films composition toward a stoichiometric value. However, the composition of films deposited at higher target rotation are found to be far from the expectation as can be seen by extremely low Cu and Zn compositions while exhibits high excessive Se. in comparison with the other films deposited using 5 rpm target rotation. In this experiment, a control of film composition was finally optimized and reproduced using deposition parameters of 60 min deposition time, $200^{\circ}C$ substrate temperature and 5 rpm target rotation.

3.2 Structure

The X-ray diffraction pattern and phase of films deposited at various substrate temperatures with 30 min deposition time and 5 rpm target rotation are shown in the Fig. 1(a). Generally speaking, by comparing lattice spacing of films with reference[6,7], all films reveal a stannite diffraction pattern with a (112) plane is the strongest reflection, along with weak (220/204) and (312/116) reflections. There are no other phases or elements were detected in the films by XRD. The intensity ratio of (112) reflection with respect to the others is remarkably higher, showing a high degree of (112) preferred orientation. At present, a basis of this phenomenon is not clear yet. It seems that a highly (112) preferred orientation might be a particular structural characteristic of chalcopyrite and Cu-based chalcopyrite quaternary compounds films deposited by PLD method[5,10,13-15]. It is worth noting that the (112) reflection is of beneficial for attaining good lattice match with CdS buffer layer in the thin film solar cell structure for attaining a cell's high efficiency[5]. The peak intensity of (220/204) reflection are found to enhance further by depositing films at longer deposition time as shown in Fig. 1(b), showing a significant effect of prolonged deposition time on the film structure. An observation on target rotation dependence of films diffraction pattern deduces that the degree of film crystallinity of (112) reflection tends to decrease slightly with an increase of target rotation, as denoted by the (112) and (220/204) peak
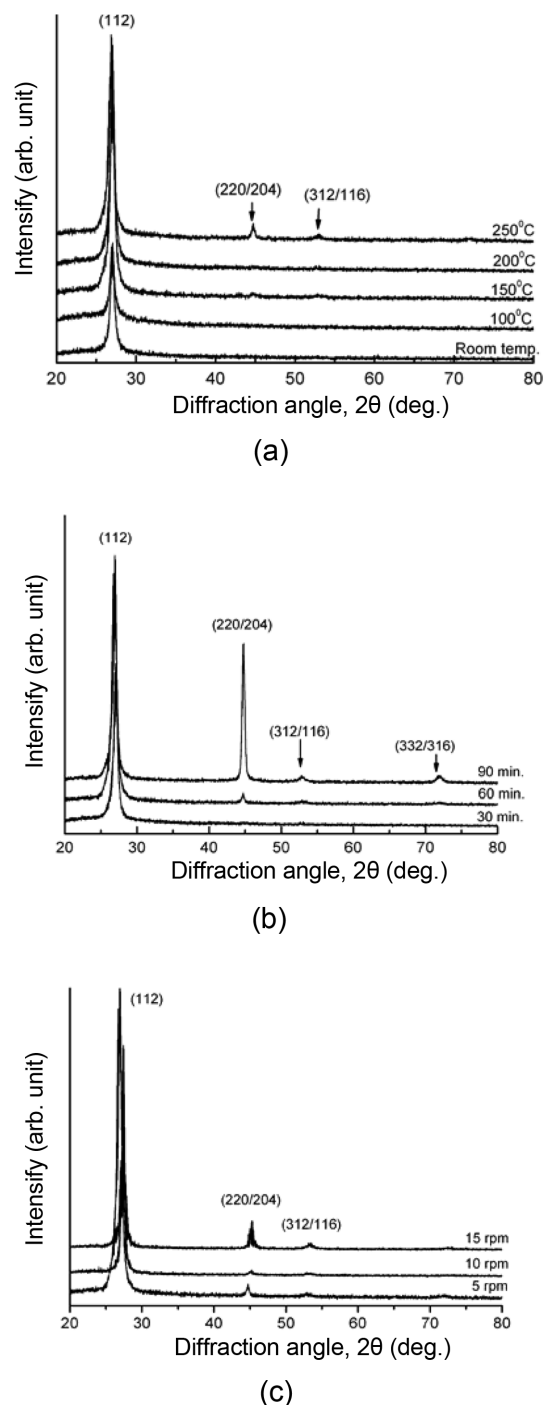

(a)

(b)

(c)

Fig. 1. X-ray diffraction patterns of films deposited using various deposition parameters; (a) 30 min deposition times, 5 rpm target rotation at various substrate temperatures, (b) 5 rpm target rotations, $200^{\circ}C$, at various deposition time, (c) 60 min, $200^{\circ}C$ at various target rotations.

intensities reduction in Fig. 1(c), probably due to off stoichiometric composition of films after deposited using higher target rotational speed. Using Scherrer's formula, $t = 0.9\lambda/\beta\cos\theta$ (t = crystallize size, λ = X-ray wavelength, β = full-width at half-maximum, and
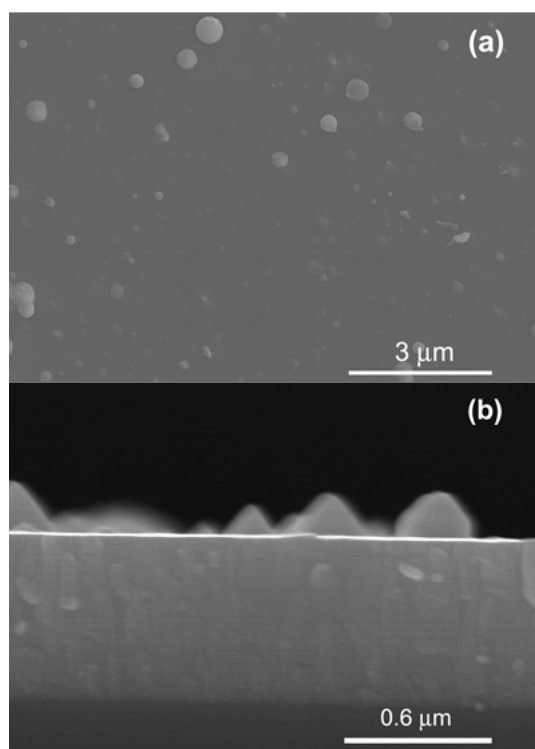
Fig. 2. Typical SEM images of Cu$_2$ZnSnSe$_4$ films; (a) surface (b) cross section.

Fig. 3. Three-dimensional AFM image of Cu$_2$ZnSnSe$_4$ film deposited at the optimum condition.

θ = Bragg angle), crystallite size for (112) reflection of the Cu$_2$ZnSnSe$_4$ thin film deposited at the optimum condition was determined approximately 22~24 nm.

3.3 Surface Morphology

Typical SEM surface image of the Cu$_2$ZnSnSe$_4$ film deposited by PLD using 5 rpm target rotation at 60 min deposition time and 200°C substrate temperature is depicted in Fig. 2(a). Smooth and dense film surface can be observed along with randomly distributed particulates on the film surface. These particulates originate from the target material by a mechanism called "splashing"[16] that occurs when the target is subjected to a subsurface explosive volume boiling during laser ablation. Particulates ejected from the target by this mechanism can be entrapped inside or on the surface of the film and is known to be a major drawback of using PLD method. In accordance with compositional examination on the particulates, they possess an identical composition with the target material. Cross sectional SEM image of film shows a smooth and dense structure with a good adhesive to the glass substrate, as shown in Fig. 2(b).

An AFM analysis was also done for a complementary investigation on film surface morphology (without the particulates) which could not clearly be resolved by an SEM analysis. Fig. 3 represents a
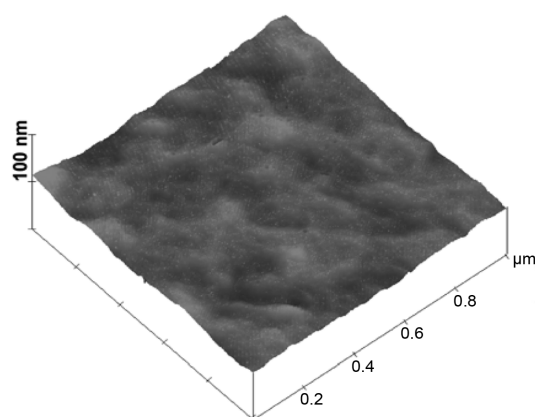
Cu$_2$ZnSnSe$_4$ film surface morphology. The film deposited at an optimum condition exhibits smooth surface roughness as denoted by a reduction in root-mean-square (RMS) value of 0.66 nm. The RMS value of films is exceptionally smooth in comparison with the Cu-based chalcopyrite quaternary compounds films deposited by other deposition method[8,9]. It can be explained when substrate temperature was elevated to 200°C, the diffusion rate of adatom is improved remarkably in comparison with no substrate heating condition therefore a film could grow in regular, smoother and more compact manners. This fact is in a good agreement with island aggregation Monte Carlo simulation as a function of substrate temperature[17].

3.4 Optical and Electrical Properties

The optical properties of pulsed laser deposited Cu$_2$ZnSnSe$_4$ films were evaluated by taking films optical transmittance at first and followed by calculating films coefficient absorption and band gap. The absorption edge for direct interband transition is given by $\alpha^2 = hv - E_g$, where h is Planck's constant, and v is the frequency of the incident photon. The coefficient of absorption α is defined as $I = I_o e^{-at}$ where I is the intensity of transmitted light, I_o is the intensity of incident light, and t is the thickness of film. The transmittance is defined as I/I_o, therefore α can be obtained. The absorption coefficient of the Cu$_2$ZnSnSe$_4$ film deposited at an optimum condition is approximately $> 1.5 \times 10^4$ cm^{-1} which is thought of satisfying the absorption coefficient requirement of a solar absorber. The optical band gap (E_g) of the film can be determined by the extrapolation methods from absorption edge. Fig. 4 shows the typical band gap of the Cu$_2$ZnSnSe$_4$ film deposited using the optimum condition. The energy gap can be obtained from the
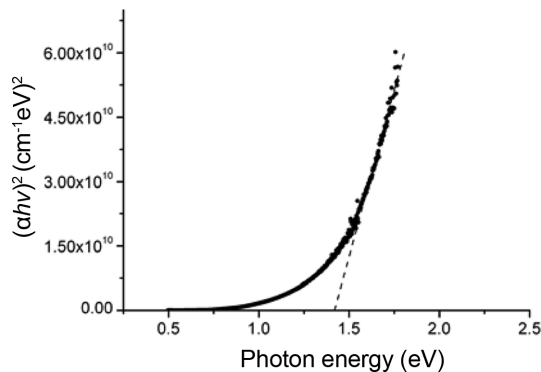
Fig. 4. Band gap of a Cu$_2$ZnSnSe$_4$ film deposited at the optimum deposition condition.

intercept of $(\alpha h\nu)^2$ vs $h\nu$, yielding a band gap of 1.45 eV. This result is consistent with the reference[6].

The electrical properties of sputtered Cu$_2$ZnSnSe$_4$ thin films deposited at an optimum condition were characterized in terms of carrier concentration n_p, Hall mobility μ_H, and resistivity ρ. The measurement was taken at 300 K. It was determined that the Cu$_2$ZnSnSe$_4$ film deposited at an optimum condition were identified as p-type semiconductor material with a carrier concentration of 1.04×10^{17} cm^{-3}, μ_H in the order of 10^1 cm^{2}V^{-1}s^{-1} and ρ of 1.8×10^{-1} Ωcm.

4. Conclusions

Nearly stoichiometric and single phase of quaternary Cu$_2$ZnSnSe$_4$ thin films were deposited by using pulsed laser deposition. Control of films composition was initially performed by varying experimental conditions of substrate temperature, deposition time and target rotational speed. In this experiment, films with a nearly stoichiometric composition were deposited and reproduced using 60 min deposition time, 5 rpm target rotation at a relatively low substrate temperature. It is generally observed that pulsed laser deposited Cu$_2$ZnSnSne$_4$ films exhibit a stannite single phase with a highly preferred (112) orientation. Surface morphology of film was observed to be dense and smooth with a presence of randomly distributed particulates. A Cu$_2$ZnSnSe$_4$ film deposited at the optimum condition demonstrated a band gap of 1.45 eV with an absorption coefficient of 10^4 cm^{-1}. The film showed a p type semiconductor characteristic with an optimum carrier concentration in order of 10^{17} cm^{-3}, μ_H of 10^1 cm^{2}V^{-1}s^{-1} and ρ of 10^{-1} Ωcm.

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