Investigation of Deposition Parameters Dependence on Sputtered Cu2ZnSnSe4 Thin Films Properties

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Investigation of Deposition Parameters Dependence on Sputtered $Cu_2ZnSnSe_4$ Thin Films Properties

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Abstract. $Cu_2ZnSnSe_4$(CZTSe) thin films were deposited by sputtering process using powder compacted target of CuSe, ZnSe and SnSe on Corning 1737 glass for Indium-free thin film solar cell application. Film composition,structure and properties were investigated by varying deposition parameters,such as substrate temperature,film thickness and RF power in order to deposit films with a stoichiometric composition and single phase of CZTSe. At an optimal condition of experiment,substrate temperature toward 150^0 C,RF power 75W, CZTSe films near stoichiometric composition with a polycrystalline stannite single phase were successfully deposited. Film thickness was little dependency with structure and composition except optical transmittance of the films. And it was observed to have a absorption coefficient of up to 10^4 cm^{-1}, band gap energy of 1.5 eV, carrier concentration in order of 10^{19} cm^{-3}, mobility of 10^0 $cm^2V^{-1}s^{-1}$ and resistivity of 10^{-1}-10^3 Ωcm.It was also showed that all films were identified as *p*-type semiconductor.

Introduction

The first report on chalcopyrite $CuInSe_2$ (CIS) thin film solar cells [1] and subsequent investigations [2] have spurred efforts to study the physical properties of chalcopyrite CIS materials. A CIS-based compound alloying with gallium ($CuIn_{1-X}Ga_XSe_2$/CIGS) is considered to be one of the promising materials for thin film solar cells exhibiting cell and module efficiencies close to 18% and 16%, respectively [3,4]. An additional Ga is incorporated with the purpose of increasing band gap energy from 1.1 to 1.5 eV thus increasing the open circuit voltage (V_{OC}) of solar cell.

However, it is realized that this absorber employs expensive materials such as In and Ga. Recently, quaternary semiconductor of Cu-based chalcopyrite compounds (Cu_2-II-IV-VI_4 , II = Zn; IV = Sn; VI= S, Se) are regarded as a promising novel material 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}[5]. CZTSe is the materials which can be synthesize by replacing half of In in chalcopyrite $CuInSe_2$ with Zn and by replacing the other half with Sn. This paper reports an optimization of thin films deposition by using sputtering method in order to obtain stoichiometric and single phase CZTSe as a potential candidate for solar absorber material in thin film solar cell. Effects of various deposition parameters were investigated and were discussed.

Experiment

In order to prepare powder compacted sputtering targets, CuSe, ZnSe and SnSe powders (each of 99.9 %) were ball-milled for 24 hours in the polyethylene container. The mole ratio was initially CuSe: ZnSe : SnSe = 2:1:1 for depositing a nearly stoichiometric CZTSe film. In this research, target composition was optimized by modifying ZnSe mole ratio to 1.2 for working against Zn loss during sputtering. In addition, the use of binary selenides as a sputtering target was expected to be acted as Se

source which avoids the difficulty of two-stage process of sputter deposition-selenization [6].Ten grams of the mixed powder were uniaxially pressed at a pressure of 5 tons in a 2 inch-diameter target holder and were employed throughout the experiments.

After initially evacuated the chamber by a rotary pump followed by a turbomolecular pump, high purity Ar gas was introduced at a constant flow rate of 100 sccm, yielding a working pressure of 6 Pa. Throughout all deposition, the target was pre-sputtered for 15 minutes before actual deposition begin in order to remove any contaminants from the target surface. In order to maintain target composition's stoichiometry and to prevent any target's surface damages, the target was regularly replaced after being sputtered. There are three variables involved in this study for preparing the near stoichiometric CZTSe composition and single phase; (1) substrate temperature ranging from no intentional substrate heating to 200^0C, (2) film thickness from 400 to 3700nm and (3) RF power from 50 to 125 W.

The determination of the films was carried out by an Energy Dispersive X-Ray Spectrometer/EDX (EMAX-Horiba, Japan) attached to a Scanning Electron Microscope/SEM (Hitachi S-4100, Japan) and X-ray diffraction/XRD(PANanalitycal,Netherlands).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 using the Van der Paw method at 300 K (ECOPIA HMS-3000, USA).

Results and discussion

The composition profile of the films as a function of substrate temperature is shown in Fig. 1.

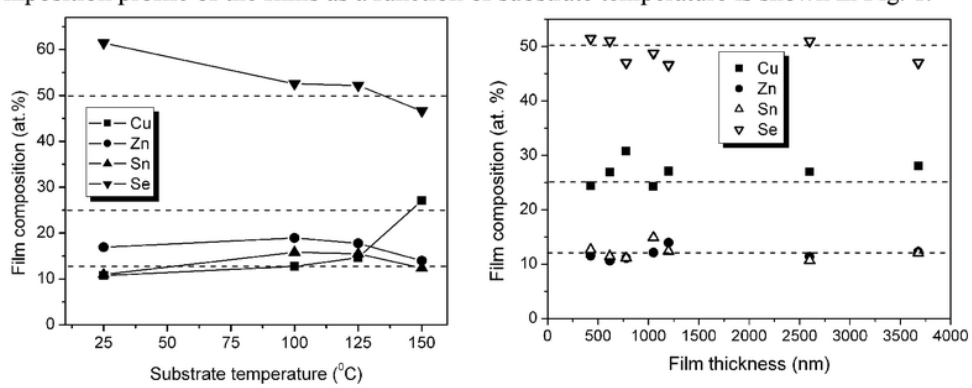

Fig. 1. Composition profile as a function of substrate temperature(left) at 1200nm thickness film and composition profile as a function of film thicknesses(right) deposited at150°C. The dotted lines represent a stoichiometric composition.

Films composition tends to alter as substrate temperature increases from no intentional heating to 150^0C. It is thought that the alteration of films composition is mainly controlled by the loss or re-evaporation of more volatile adatoms, in this case Se, during deposition at a higher substrate temperature. Cu concentration in the film tends to increase with a decrease of Se concentration while Zn and Sn concentrations relatively maintained their stoichiometric composition. At 150^0C, films with approximate stoichiometric mole ratio of Cu/(Zn+Sn) = 1.03, Zn/Sn = 1.13, and Se/(Cu+Zn+Sn) = 0.87 were successfully deposited and reproduced. Experiments done at temperature beyond 150^0C, yielded films with highly excessive Cu and Se deficient, deduces a temperature optimization at 150^0C.

The compositional uniformity of the films was also investigated over various film thicknesses deposited at 150°C. As can be seen in Fig. 1(right), the films could be deposited at relatively uniform composition independent with film thickness with some degrees of Cu and Se non stoichiometry near 750nm thickness. From the compositional profile of Fig.1, it is obvious that the Cu concentration is related with Se concentration; as Se concentration decreases, Cu concentration tends to increases

proportionally. It is worth noting to emphasize that either moderate Se concentration excess or deficiency can be tolerated since it does not affect significantly to the formation of quaternary Cu-based chalcopyrite compounds [7].

In addition, experimental works revealed that films composition near stoichiometry could be controlled by using low RF power. The use of 50 and 75 W RF powers still maintain the composition of films at near stoichiometric, whereas the use of higher RF powers of 100 and 125 W led to an abrupt change of the films composition far from stoichiometric (data were not shown).

A typical X-ray diffraction pattern of the films as a function of substrate temperature and film thickness is demonstrated in Fig.2.

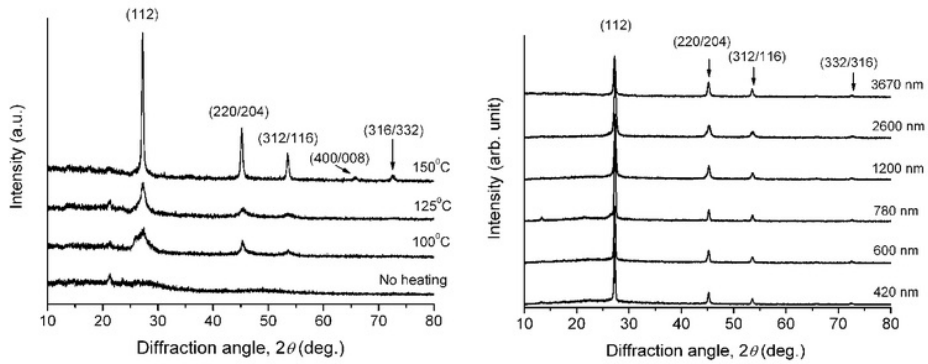

Fig. 2. X-ray diffraction pattern of CZTSe films with 1200nm thickness deposited at various temperatures(left) and X-ray diffraction pattern of CZTSe films with various film thickness(right) at RF power 75 W,150^{0}C .

The peak intensity of stannite (112), (220/204) and (312/116) reflections is revealed to be enhanced proportionally with an increase of substrate temperature. The films deposited at 150^{0}C also demonstrate a highly polycrystalline of films, denotes by a more complete series of stannite phase reflections of (112), (220/204), (312/116) along with very weak (400/008) and (332/316) reflections. No elements or other phases were detected on the films using XRD. It has been well-known that the chalcopyrite and quaternary Cu-based chalcopyrite compounds thin films posses a large structural tolerance to cation-anion off-stoichiometry [8]. The results in this work are in a good agreement with the abovementioned reports. The improvement of degree of crystallinity of films deposited at higher substrate temperature can be thought to be a result of two major factors; (1) films composition alteration toward a Cu-rich composition and (2) a re-crystallization of films. A near stoichiometric composition of films leads to a complete CZTSe reaction of each element which ultimately yields more exact structure of film. Moreover, an increasing substrate temperature always provides the additional energy for sputtered adatoms to enhance further nucleation and re-crystallization [9].

The X-ray diffraction pattern of films deposited at different thickness maintains a polycrystalline stannite single phase in Fig. 2(right).As can be observed, a stannite phase of film is stable over a wide range of thickness, without any presence of other phases that could probably be grown after a prolonged deposition time to reach thicker films. A slight increase of peak intensities of stannite phase is found to occur on all (112), (220/204) and (312/316) reflections. The enhancement of films degree of crystallinity is due to an increase of film thickness. As a film gets thicker, the grains of the films also grow further, hence the final size of grains deposited at a thicker film is supposed to be larger than that of a thinner one. 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 θ = Bragg angle), crystallite size of CZTSe thin film deposited at 150^{0}C for (112) reflection was determined approximately 25 nm, which is close to grain size of Müller et al. after depositing CIS thin films using a single CIS sputtering target [8].

Typical surface and cross section images of CZTSe films deposited at 150^{0}C are represented in Fig. 3. Surface image of CZTSe film shows uniformly distributed facetted grains with a number of grain

boundaries in Fig.5(a). Cross sectional SEM images of sputtered CZTSe film show a typical columnar structure in Fig.3(b). The films were observed to be uniform and possess a densely packed columnar structure.

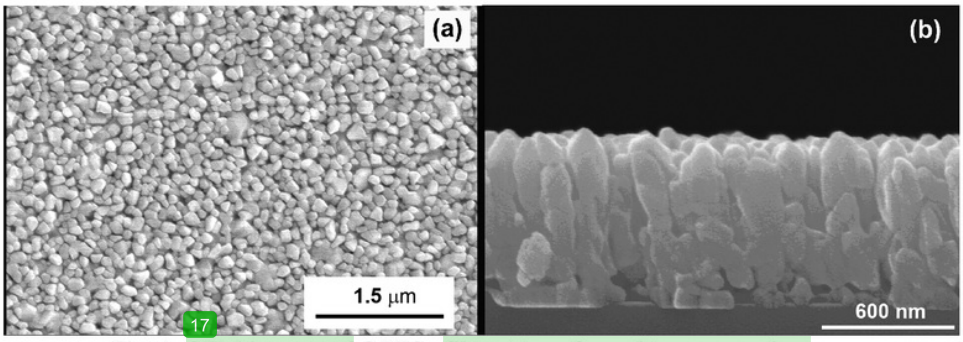

Fig. 3. SEM images of CZTSe film; (a) surface, (b) cross section.

The optical characteristics of the films were evaluated in terms of the optical transmission spectra, absorption coefficient and photon energy in Fig.4.

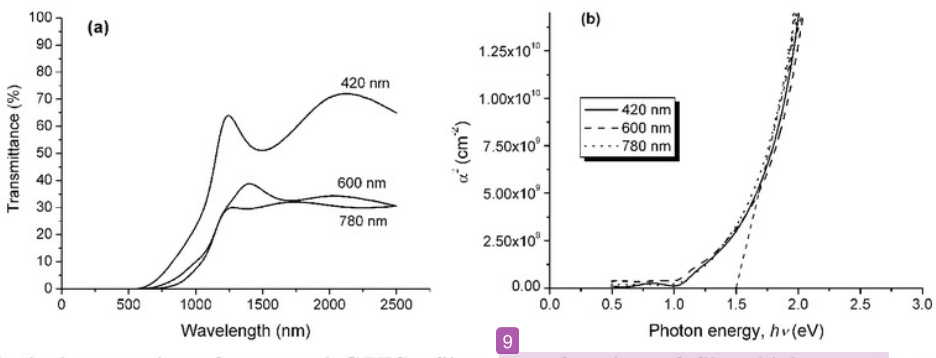

Fig 4. Optical properties of sputtered CZTSe films as a function of film thickness; (a) optical transmittance, (b) photon energy.

Fig.4(a) shows the typical optical transmittance of CZTSe films with various film thicknesses deposited at 150^{0}C.It is clearly seen that the optical transmittance reduces gradually with an increase of film thickness. The decrease of optical transmittance is thought be the result of generation of reflection due to the optical paths in a thin film [10]. The optical band gap (E_g) of the film can be determined by the extrapolation methods 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 $I = I_o e^{-\alpha d}$ 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 CZTSe films was determined to be approximately >1.5 x 10^4 cm^{-1}. Fig. 4(b) is the plot of α^2 vs $h\nu$. The band gap energy can be obtained from the intercept of α^2 vs $h\nu$, yielding a band gap of 1.5 eV at various film thickness.

Hall measurement analysis reveals CZTSe thin films were identified as p-type semiconductor with a carrier concentration in order of 10^{19} cm^{-3}, mobility (μ_H) of 10^0 cm^{2}V^{-1}s^{-1} and resistivity (ρ) of 10^{-1}-10^3 Ωcm. The hole mobility was found to be small in comparison with the hole mobility of a Cu(In,Ga)Se$_2$ film. It is discussed earlier that the CZTSe thin films possess small grains, which means exhibit a number of grain boundaries. These grain boundaries may act as a defect in films that inhibit the mobility of carriers/holes according to Mathiessen's rule [11]. Nevertheless, for a device operation,

mobility through-the-grain values are more relevant, since individual grains may extend from the back contact to the interface of junction [12].

Conclusion

$Cu_2ZnSnSe_4$ thin films were successfully deposited by sputtering process using powder compacted target composed of CuSe, ZnSe and SnSe compounds. The effects of deposition parameters on the properties were investigated. At the optimal deposition parameter and condition,ie,substrate temperature toward 150^0 C and RF power 75W, CZTSe films near stoichiometric composition with a polycrystalline stannite single phase were successfully deposited. Film thickness was in little dependency with structure and composition except optical transmittance of the films. Absorption coefficient was determined to be approximately >1.5 x 10^4 $cm^{-1}$and band gap energy was 1.5 eV, which is believed to be matched with the properties of a solar absorber material. CZTSe thin films were identified as *p*-type semiconductor with a carrier concentration in order of 10^{19} cm^{-3}, mobility of 10^0 $cm^2V^{-1}s^{-1}$ and resistivity of 10^{-1}-10^3 Ωcm.

Acknowledgment

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