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Preparation of High Ga Content $Cu(In,Ga)Se_2$ Thin Films by Sequential Evaporation Process Added In_2S_3

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ABSTRACT

High Ga content $Cu(In,Ga)Se_2$ thin films incorporated sulfur were prepared by sequential evaporation from $CuGaSe_2$ and $CuInSe_2$ ternary compounds and subsequently Ga_2Se_3, In_2Se_3 and In_2S_3 binary compounds. The $In_2S_3/(Ga_2Se_3+ In_2Se_3)$ ratio was varied from 0 to 0.13, and the properties of the thin films were investigated. XRD studies demonstrated that the prepared thin films had a chalcopyrite $Cu(In,Ga)Se_2$ structure. The S/(Se+S) mole ratio in the thin films was within the range from 0 to 0.04. The band gaps of $Cu(In,Ga)Se_2$ thin films increased from 1.30 eV to 1.59 eV with increasing the In_2S_3 /$(Ga_2Se_3+ In_2Se_3)$ ratio.

Keywords: Cu(In,Ga)Se2 Thin Film; Solar Cell; High Ga Content; Sulfur Incorporation; Sequential Evaporation

1. Introduction

Photovoltaic power system has received considerable attention for safety and clean energy resources. It is necessary to fabricate low cost and high efficient solar cells in order to spread the PV system widely. Chalcopyrite $Cu(In,Ga)Se_2$ is a potential absorber material for high efficiency thin film solar cell because of its favorable band gap and high absorption coefficient for solar radiation. The band gap energy of $Cu(In,Ga)Se_2$ thin films varies from about 1.0eV to 1.7eV according to the increase in $CuGaSe_2$ molar fraction which makes it also promising for single-junction and multi-junction solar cell applications [1]. Conversion efficiencies for $Cu(In,Ga)Se_2$ based solar cells have been significantly improved over recent years and achieved the value of 20% by three-stage process using a multisource vacuum evaporation system equipped with elemental Cu, In, Ga and Se sources [2,3]. The Ga/(In+Ga) ratio of this absorber was around 0.3, which showed a band gap Eg of about 1.14 eV. It is expected to improve the efficiency by increasing its band gap until 1.4 eV due to a better matching solar spectrum. The conversion efficiencies of $Cu(In,Ga)Se_2$ thin film solar cells decreased with increasing a Ga/(In+Ga) mole ratio above 0.3 [4]. For example, the efficiencies of $Cu(In,Ga)Se_2$ thin film solar cells were 12% for Ga/(In+Ga) mole ratio of 0.73 (Eg=1.5 eV) and 10% for that of 0.91 (Eg=1.62 eV), respectively [4]. On the other hand, a performance of $Cu(In,Ga)Se_2$ thin film solar cell with a Ga/(In+Ga) mole ratio of around 0.3 was improved by sulfurization of the film surface such as InS treatment by a wet process [5] and annealing in S vapor atmosphere [6]. We have proposed the process using a vacuum deposition apparatus with three evaporation boats which was the sequential evaporation technology from $CuGaSe_2$ and $CuInSe_2$ ternary compounds [7,8]. Our proposed process has advantages to be able to easily control a Ga/(In+Ga) mole ratio in $Cu(In,Ga)Se_2$ thin films by changing the amount of $CuGaSe_2$ and $CuInSe_2$ evaporating materials in the first step and to use inexpensive equipment for preparation of an absorber layer. In this study, one evaporation source was added in our vacuum deposition apparatus. In_2S_3 was added as an evaporation material in the third step of our sequential evaporation process and the prepared thin films and solar cells were investigated.

2. Experimental

2.1. Preparation of $Cu(In,Ga)Se_2$ Thin Films Added In_2S_3

The evaporating materials of $CuGaSe_2$ and $CuInSe_2$ were synthesized by reacting stoichiometric amounts of high-purity elements (Cu, In, Ga, Se) in sealed and evacuated quartz ampoules. The detail procedure was described in Reference [9]. The $CuInSe_2$ and $CuGaSe_2$ ingots were removed from the quartz ampoules. In_2Se_3, Ga_2Se_3 and In_2S_3 compounds available in the market were used as an evaporating material. Mo layer used as a back contact was prepared by rf magnetron sputtering onto soda-lime glass substrate in Ar ambient. Our evaporation process consists of the four steps, which schematic profile was shown in **Figure 1**. Before fabrication of $Cu(In,Ga)Se_2$ thin films, the Mo/soda-lime glass substrates were heated in vacuum for 5min at 500^{o}C with infrared lamp. After cooling down to 200^{o}C, in the first step, Cu-In-Ga-Se layer was evaporated from $CuGaSe_2$ and $CuInSe_2$ compounds onto the Mo/soda-lime glass. The $CuGaSe_2/(CuGaSe_2+ CuInSe_2)$ mole ratio of the evaporating materials kept at constant of 0.8. In the second step, In-Ga-Se layer was deposited from In_2Se_3 and Ga_2Se_3 compounds at a substrate temperature of 490^{o}C. The $(In_2Se_3 + Ga_2Se_3)$/ $(CuGaSe_2 + CuInSe_2)$ mole ratio kept at constant of 0.2. In the third step, S was deposited from In_2S_3 compound at a substrate temperature of 490^{o}C.The $In_2S_3/(In_2Se_3+Ga_2Se_3)$ mole ratio was varied from 0 to 0.13 in this experiment. Finally, only Se was effused at the same substrate temperature.

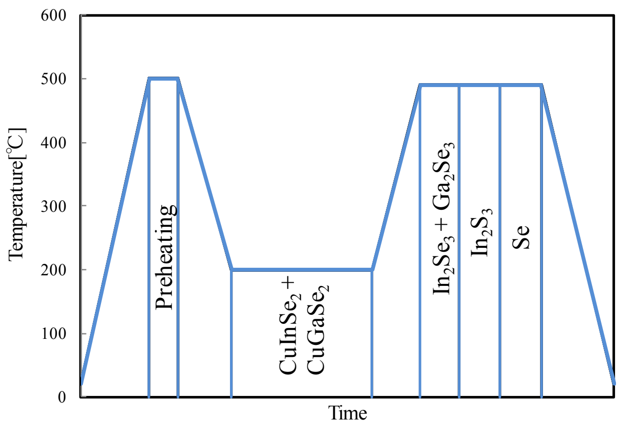

Figure 1. Schematic profile of our sequential evaporation process.

2.2. Fabrication of Solar Cells

The solar cells with a configuration of Al/ZnO:Al/i-ZnO/CdS/ Cu(In,Ga)Se_2/Mo/SLG substrate were fabricated. CdS buffer layer with a thickness of 70 nm was deposited by the chemical bath deposition technique using a CdI_2 (2.0x10^{-3} M)-thiourea (0.166M)- ammonia (1M) aqueous solution during heating from room temperature to 65°C. i-ZnO buffer layer with a thickness of 100 nm was deposited by rf-magnetron sputtering from non-doped ZnO target in Ar gas at room temperature. Transparent conductive ZnO:Al film with a thickness of 0.4 μm was subsequently deposited by rf-magnetron sputtering from a 2wt%Al_2O_3 doped ZnO target in Ar gas at room temperature. Al grids for the front electrode were formed by a vacuum evaporation with W boat using a metal mask. No antireflection coating was applied. The size of a solar cell is 5 mm x 5 mm.

2.3. Characterization

The surface composition of thin films were determined by an electron probe microanalysis (EPMA). The effective range of electron for production of the characteristic X-rays in EPMA analysis is roughly estimated to be around 0.4 μm for Cu (In,Ga)Se_2 thin films [10]. The growth orientation of thin films was studied by X-ray diffraction (XRD) in the θ-2θ mode using Cu Kα radiation. The surface and cross-section morphology and grain size of the thin films were studied by scanning electron microscopy (SEM). Current-voltage characteristics of solar cells were measured using standard 1-sun (AM1.5, 100mW/cm^2) illumination. The quantum efficiencies of solar cells were measured using a spectrophotometer with illumination normalized against calibrated photodiode.

3. Results and Discussion

3.1. Film Composition

From EPMA analysis, the thin films prepared at various In_2S_3/ (In_2Se_3+Ga_2Se_3) mole ratio had almost a stoichiometry composition in I-III-VI_2 compound. **Figure 2** shows the compositional ratio of Ga/(In+Ga) and S/(Se+S) in the thin films. In this experiment, the $CuGaSe_2$/($CuGaSe_2$+$CuInSe_2$) mole ratio in the evaporating materials was kept at constant of 0.8. The Ga/(In + Ga) mole ratio in the thin films prepared in the range of In_2S_3/ (In_2Se_3+Ga_2Se_3) mole ratio from 0 to 0.13 was within the range from 0.855 to 0.747. The Ga/(In+Ga) mole ratio slightly decreased with increasing the In_2S_3/(In_2Se_3+Ga_2Se_3) mole ratio due to the presence of In in the third step. These values are considered to be a high Ga content which is the purpose of this study. On the other hand, the S/(Se+S) mole ratio in the tin films increased from 0 to 0.04 with increasing the In_2S_3/(In_2Se_3 + Ga_2Se_3) mole ratio. A slightly S incorporation into the thin films was confirmed from EPMA analysis.

3.2. Crystal Structure

Figure 3 shows XRD patterns for the thin films prepared at In_2S_3/(In_2Se_3+Ga_2Se_3) mole ratio of 0 to 0.13. XRD spectrum exhibited several peaks corresponding to diffraction lines of the chalcopyrite phase in Cu(In,Ga)Se_2, in particular split of 220/204 and 312/116 diffraction lines. The 112 diffraction line was the strongest. The position of X-ray diffraction peaks for Cu(In,Ga)Se_2 thin films prepared at various In_2S_3/(In_2Se_3 + Ga_2Se_3) mole ratio was almost same although the Ga/(In+Ga) and S/(Se+S) mole ratio in the thin films was slightly different.

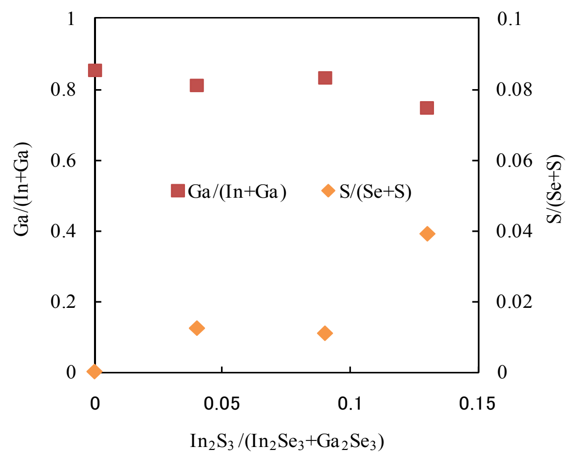

Figure 2. Compositional ratio of the prepared thin films determined by EPMA.

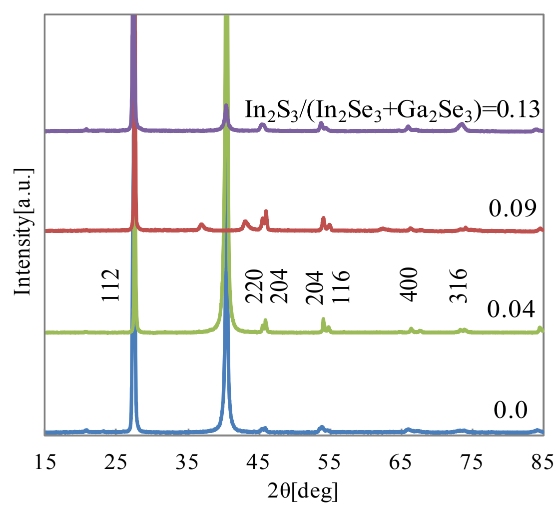

Figure 3. XRD patterns of the thin film prepared at In_2S_3/(In_2Se_3+ Ga_2Se_3)=0- 0.13.

3.3. Grain Size

SEM micrographs of the cross section of Cu(In,Ga)Se_2 thin films prepared at In_2S_3/(In_2Se_3+Ga_2Se_3) mole ratio of 0 to 0.13 are shown in **Figure 4**. This Cu(In,Ga)Se_2 thin films had a high Ga content such as Ga/(In+Ga) mole ratio of the range from 0.855 to 0.747. The grain size in Cu(In,Ga)Se_2 thin film was estimated to be smaller than 1.0 µm. It is well known in general that efficiencies of polycrystalline solar cells increase with increasing grain sizes in the absorber materials. Therefore, the large grain growth in Cu(In,Ga)Se_2 thin films is required for the fabrication of high-performance photovoltaic devices. In comparison with **Figures 4(a)** and **(b)**, the grain size in **Figure 4(b)** was seemed to be larger than that in **Figure 4(a)**, suggesting the promotion of the grain growth by slightly In_2S_3 supplying.

3.4. Band gap Engineering

The solar cells with a configuration of ZnO: Al/i-ZnO/CdS/Cu (In,Ga)Se_2/Mo/soda-lime glass substrate were fabricated by using Cu(In,Ga)Se_2 thin films prepared at In_2S_3/(In_2Se_3 + Ga_2Se_3) = 0-0.13. The best solar cell demonstrated V_{oc}=500mV, I_{sc}= 19.07mA/cm^2, FF = 0.39 and η = 4.1% without AR-coating, which used Cu(In,Ga)Se_2 thin film prepared at In_2S_3/(In_2Se_3 + Ga_2Se_3)=0.04. The efficiencies for Cu(In,Ga)Se_2 thin film solar cells were not so good. However, the remarkable change was observed in the quantum efficiency of Cu(In,Ga)Se_2 thin film solar cells, which was shown in **Figure 5**. The quantum efficiency from 400 nm to 600nm for Cu(In,Ga)Se_2 thin film solar cells prepared at In_2S_3/(In_2Se_3+Ga_2Se_3) = 0.04 and 0.09 increased rather than that at In_2S_3/(In_2Se_3+Ga_2Se_3) = 0. Moreover, the absorption band edge in the long wavelength region shifted to the short wavelength range with increasing In_2S_3/(In_2Se_3+ Ga_2Se_3) mole ratio. For a direct transition, the dependence of the absorption coefficient α on the photon energy hν is given by

$$\alpha h\nu = A(h\nu - Eg)^{1/2} \quad (1)$$

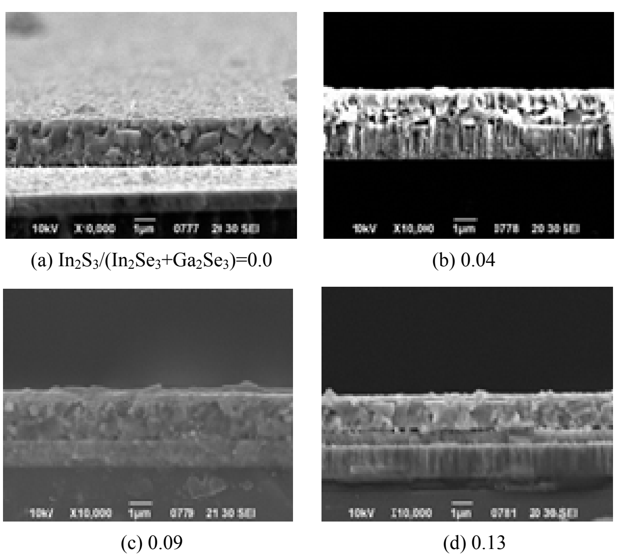

Figure 4. SEM micrographs of the cross-section of Cu(In,Ga)Se_2 thin films prepared at In_2S_3/(In_2Se_3+Ga_2Se_3) =0-0.13.

Assuming a very short minority carrier diffusion length Ln, the quantum efficiency QE can be approximated by

$$QE = 1 - \exp(-\alpha W) \quad (2)$$

where W is the width of the space charge region. From euqations (1) and (2), the following equation is deduced

$$\ln(1 - QE) \times h\nu = -WA(h\nu - Eg)^{1/2} \quad (3)$$

so that a plot of [hν xIn(1-QE)]^2 against hν can be used to extrapolate the band gap Eg [11]. From this manner, the band gaps estimated from the QE spectra were changed from 1.30 eV to 1.59 eV, which shown in **Figure 6** including the open circuit voltage V_{oc} of Cu(In,Ga)Se_2 thin film solar cells. The value of band gap is expected to be 1.56eV for Cu(In,Ga)Se_2 thin film with Ga/III=0.855 from the data reported by Paulson et al [12]. However, the band gap of 1.30eV obtained from Cu(In,Ga)Se_2 thin film prepared at In_2S_3/(In_2Se_3+Ga_2Se_3)=0 in this experiment was extremely a small value. It has been reported that efficient Cu(In,Ga)Se_2 thin film solar cells with Ga/(In+Ga) mole ratio of 0.3 fabricated by three stage process had a double

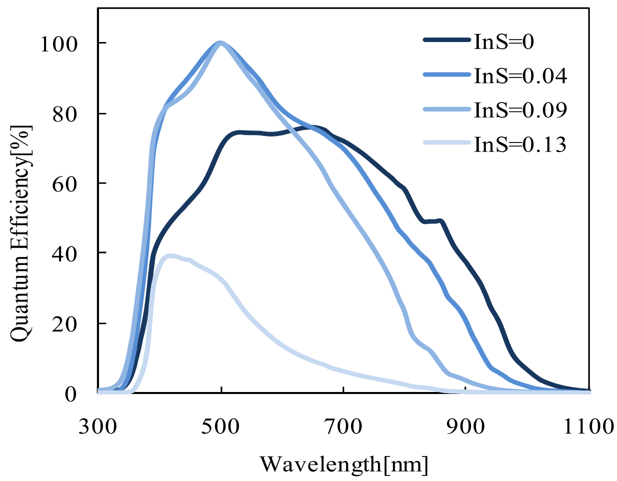

Figure 5. Quantum efficiency of Cu(In,Ga)Se_2 thin film solar cells prepared at In_2S_3/(In_2Se_3+Ga_2Se_3)=0-0.13.

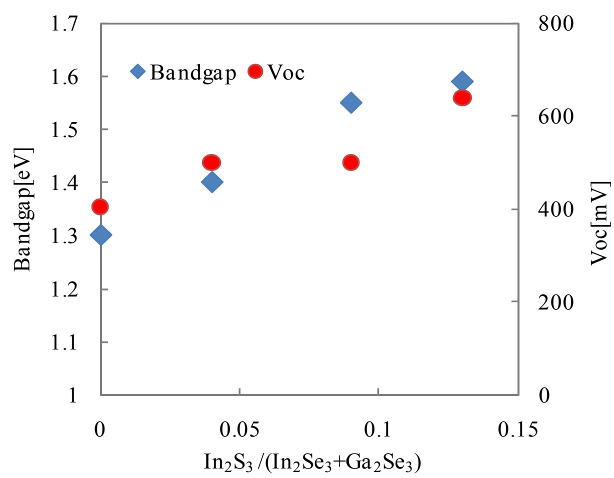

Figure 6. Dependence of band gap and open circuit voltage on In_2S_3/(In_2Se_3+Ga_2Se_3) mole ratio.

graded band gap structure [13]. Therefore, it is presumed that the value of 1.3 eV demonstrates the bottom of the double graded band gap structure. This result is suggestive that Cu $(In,Ga)Se_2$ thin film solar cells with a high Ga/(In+Ga) mole ratio have a deep valley structure. The deep valley prevents the carrier collection and causes the deterioration of solar cell performance. The similar tendency for $Cu(In,Ga)Se_2$ thin film solar cells with Ga/(In+Ga) mole ratio of 0.3 fabricated on Mo coated Ti foils by three stage process has been reported [14]. On the other hand, $Cu(In,Ga)Se_2$ thin film prepared at In_2S_3/ $(In_2Se_3+Ga_2Se_3)$=0.04 demonstrated a band gap of 1.4 eV, which was suitable for a better matching solar spectrum. Thus the cell performance was improved. Therefore, In_2S_3 slightly supplying is one of the promising methods to improve the performance of $Cu(In,Ga)Se_2$ thin film solar cells.

4. Conclusion

For photovoltaic device applications, $Cu(In,Ga)Se_2$ thin films were prepared by sequential evaporation process. The effect of In_2S_3 supplying in the third step was examined. XRD study showed that $Cu(In,Ga)Se_2$ thin films had a chalcopyrite structure. EPMA analysis demonstrated that $Cu(In,Ga)Se_2$ thin films have Ga/(In+Ga) mole ratio of 0.855-0.747 and S/(Se+S) mole ratio of 0-0.04. From SEM micrograph, $Cu(In,Ga)Se_2$ thin films were formed with small grains. From the quantum efficiency analysis, $Cu(In,Ga)Se_2$ thin film solar cells with a high Ga/ (In+Ga) mole ratio prepared by sequential evaporation process had a deep valley structure, which was the most remarkable point in this study. This result indicates that it is expected to obtain the improvement in $Cu(In,Ga)Se_2$ thin film solar cells with a high Ga/(In+Ga) mole ratio by controlling an adequate double graded band gap structure. The performance of Cu $(In,Ga)Se_2$ thin film solar cell was improved by using slightly In_2S_3 compound in the third step.

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