Preparation of High Ga Content Cu(In,Ga)Se₂ Thin Films by Sequential Evaporation Process Added In₂S₃

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ABSTRACT

High Ga content Cu(In,Ga)Se₂ thin films incorporated sulfur were prepared by sequential evaporation from CuGaSe₂ and CuInSe₂ ternary compounds and subsequently Ga₂Se₃, In₂Se₃ and In₂S₃ binary compounds. The In₂S₃/(Ga₂Se₃+In₂Se₃) 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)Se₂ 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)Se₂ thin films increased from 1.30 eV to 1.59 eV with increasing the In₂S₃/(Ga₂Se₃+In₂Se₃) 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)Se₂ 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)Se₂ thin films varies from about 1.0 eV to 1.7 eV according to the increase in CuGaSe₂ molar fraction which makes it also promising for single-junction and multi-junction solar cell applications [1]. Conversion efficiencies for Cu(In,Ga)Se₂ 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)Se₂ 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)Se₂ 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)Se₂ 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 CuGaSe₂ and CuInSe₂ 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)Se₂ thin films by changing the amount of CuGaSe₂ and CuInSe₂ 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. In₂S₃ was added as an evaporant 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)Se₂ Thin Films Added In₂S₃

The evaporating materials of CuGaSe₂ and CuInSe₂ 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 CuInSe₂ and CuGaSe₂ ingots were removed from the quartz ampoules. In₂Se₃, Ga₂Se₃ and In₂S₃ 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)Se₂ thin films, the Mo/soda-lime glass substrates were heated in vacuum for 5 min at 500°C with infrared lamp. After cooling down to 200°C, in the first step, Cu-In-Ga-Se layer was evaporated from CuGaSe₂ and CuInSe₂ compounds onto the Mo/soda-lime glass. The CuGaSe₂/CuInSe₂ mole ratio of the evaporating materials kept at constant of 0.8. In the second step, In-Ga-Se layer was deposited from In₂Se₃ and Ga₂Se₃ compounds at a substrate temperature of 490°C. The (In₂Se₃ + Ga₂Se₃)/ (CuGaSe₂ + CuInSe₂) mole ratio kept at constant of 0.2. In the third step, S was deposited from In₂S₃ on the substrate temperature of 490°C. The In₂S₃/(In₂Se₃+Ga₂Se₃) mole ratio was varied from 0 to 0.13 in this experiment. Finally, only Se was effused at the same substrate temperature.
2.2. Fabrication of Solar Cells

The solar cells with a configuration of Al/ZnO:Al/i-ZnO/CdS/Cu(In,Ga)Se2/Mo/SLG substrate were fabricated. CdS buffer layer with a thickness of 70 nm was deposited by the chemical bath deposition technique using a CdI2 (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%Al2O3 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)Se2 thin films [10]. The growth orientation of thin films was studied by X-ray diffraction (XRD) in the 0-2θ 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/cm²) 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 In2S3/(In2Se3+Ga2Se3) mole ratio had almost a stoichiometry composition in I-III-VI2 compound. Figure 2 shows the compositional ratio of Ga/(In+Ga) and S/(Se+S) in the thin films. In this experiment, the CuGaSe2/(CuGaSe2+CulnSe2) 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 In2S3/(In2Se3+Ga2Se3) (In2Se3+Ga2Se3) 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 In2S3/(In2Se3+Ga2Se3) 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 thin films increased from 0 to 0.04 with increasing the In2S3/(In2Se3+Ga2Se3) 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 In2S3/(In2Se3+Ga2Se3) mole ratio of 0 to 0.13. XRD spectrum exhibited several peaks corresponding to diffraction lines of the chalcopyrite phase in Cu(In,Ga)Se2, 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)Se2 thin films prepared at various In2S3/(In2Se3+Ga2Se3) mole ratio was almost same although the Ga/(In+Ga) and S/(Se+S) mole ratio in the thin films was slightly different.
3.3. Grain Size

SEM micrographs of the cross section of Cu(In,Ga)Se₂ thin films prepared at In₂S₃/(In₂Se₃+Ga₂Se₃) mole ratio of 0 to 0.13 are shown in Figure 4. This Cu(In,Ga)Se₂ 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)Se₂ 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)Se₂ 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 In₂S₃ supplying.

3.4. Band gap Engineering

The solar cells with a configuration of ZnO: Al/i-ZnO/CdS/Cu (In,Ga)Se₂/Mo/soda-lime glass substrate were fabricated by using Cu(In,Ga)Se₂ thin films prepared at In₂S₃/(In₂Se₃+Ga₂Se₃) = 0-0.13. The best solar cell demonstrated Vₒc=500mV, Iₒsc= 19.07mA/cm², FF = 0.39 and η = 4.1% without AR-coating, which used Cu(In,Ga)Se₂ thin film prepared at In₂S₃/(In₂Se₃+Ga₂Se₃)=0.04. The efficiencies for Cu(In,Ga)Se₂ thin film solar cells were not so good. However, the remarkable change was observed in the quantum efficiency of Cu(In,Ga)Se₂ thin film solar cells, which was shown in Figure 5. The quantum efficiency from 400 nm to 600nm for Cu(In,Ga)Se₂ thin film solar cells prepared at In₂S₃/(In₂Se₃+Ga₂Se₃) = 0.04 and 0.09 increased rather than that at In₂S₃/(In₂Se₃+Ga₂Se₃) = 0. Moreover, the absorption band edge in the long wavelength region shifted to the short wavelength range with increasing In₂S₃/(In₂Se₃+Ga₂Se₃) mole ratio. For a direct transition, the dependence of the absorption coefficient α on the photon energy hν is given by

\[ αν = A(hν - Eg)^{1/2} \]  

(1)

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

\[ QE = 1 - \exp(-αW) \]  

(2)

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

\[ \ln(1 - QE) \times hν = -WA(hν - Eg)^{1/2} \]  

(3)

so that a plot of \( [hν \times \ln(1-QE)]^2 \) 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 Vₒc of Cu(In,Ga)Se₂ thin film solar cells. The value of band gap is expected to be 1.56eV for Cu(In,Ga)Se₂ 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)Se₂ thin film prepared at In₂S₃/(In₂Se₃+Ga₂Se₃)=0 in this experiment was extremely a small value. It has been reported that efficient Cu(In,Ga)Se₂ thin film solar cells with Ga/(In+Ga) mole ratio of 0.3 fabricated by three stage process had a double...
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)Se₂ 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)Se₂ 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)Se₂ thin film prepared at In₂S₃/(In₂Se₃+Ga₂Se₃)=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, In₂S₃ slightly supplying is one of the promising methods to improve the performance of Cu(In,Ga)Se₂ thin film solar cells.

4. Conclusion

For photovoltaic device applications, Cu(In,Ga)Se₂ thin films were prepared by sequential evaporation process. The effect of In₂S₃ supplying in the third step was examined. XRD study showed that Cu(In,Ga)Se₂ thin films had a chalcopyrite structure. EPMA analysis demonstrated that Cu(In,Ga)Se₂ 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)Se₂ thin films were formed with small grains. From the quantum efficiency analysis, Cu(In,Ga)Se₂ 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)Se₂ 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)Se₂ thin film solar cell was improved by using slightly In₂S₃ compound in the third step.

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