A simple non-toxic simultaneous selenization/sulfurization process for Cu (In, Ga)(S, Se)2 solar cells

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HIGHLIGHTS

- A non-toxic one-stage selenization/sulfurization process to produce CIGSSe solar cells.
- Sulfur content of the surface absorber layer is higher than inside when S/(S + Se) ratio ≥ 0.12.
- Maximum cell efficiency of 12.8% was achieved when the S/(S + Se) ratio was 0.12.
- Cell efficiency is close to two-stage selenization/sulfurization process based on toxic H2Se/H2S gases.

GRAPHICAL ABSTRACT

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ABSTRACT

This paper proposes a non-toxic simultaneous selenization/sulfurization process to produce Cu(In,Ga)(S,Se)2 (CIGSSe) solar cells without the need for the conventional two-stage process using toxic H2Se/H2S gases. The absorber layer is applied via sputtering with Cu-In-Ga ternary targets, whereupon non-toxic selenium and sulfur vapor are introduced simultaneously to produce chalcopyrite CIGSSe film. Experiment results demonstrate that the total sulfur content of the absorber layer increases with an increase in the S/(S + Se) ratio. When the S/(S + Se) ratio ≥ 0.12, the sulfur content of the surface absorber layer is higher than inside the sample. This contributes to an increase in the surface energy gap and Voc of the solar cell. However, an excessively high S/(S + Se) ratio can undermine the crystallinity of the CIGSSe while introducing phase segregation at the surface of the absorber layer as well as ordered vacancy compounds (OVCs) and secondary phases, which can decrease cell efficiency. A suitable proportion of sulfur in the absorber layer can inhibit excessive growth of the Mo(S,Se)2 layer and thereby enhance cell efficiency. A small number of CuGaSe2 grains were observed at the bottom of the CIGSSe absorber layer in specimens with various S/(S + Se) ratios. A maximum cell efficiency of 12.8% was achieved when the S/(S + Se) ratio was 0.12. This cell efficiency is close to the reference specimen fabricated using a two-stage selenization/sulfurization process based on toxic H2Se/H2S gases.

1. Introduction

Current developments in Cu(In,Ga)Se2 (CIGS) solar cells are aimed primarily at reducing material costs and improving cell efficiency. CIGS is a direct energy gap material, which means that it has a high absorption coefficient and high cell efficiency. Furthermore, the energy
The gap of CIGS absorber layer can be boosted by increasing the sulfur content to increase $V_{OC}$ [1–3]. This also improves the absorber layer and energy band offset at the CdS boundary [4], thereby enhancing the efficiency of the resulting CIGS solar cell. However, adding excessive sulfur may affect p–n heterojunction, which may increase the series resistance of solar cells, and decrease FF. Too great an energy gap can result in deep-level defects, and this can decrease total cell efficiency [3,5]. The gases used in the selenization and sulfurization of CIGS solar cells are H$_2$Se/H$_2$S gas and selenium/sulfur vapor. Kim et al. [6] described a simultaneous selenization and sulfurization process for homogeneous through-film Ga composition in Cu(InGa)(Se,S)$_2$ films by simultaneous H$_2$Se/H$_2$S reaction of Cu-Ga-In precursor. Annealing processes can be divided into selenization followed by sulfurization (two-stage) and simultaneous selenization/sulfurization (one-stage). At present, the method that uses H$_2$Se gas for selenization followed by H$_2$S gas for sulfurization results in superior cell efficiency. Employing this approach, Goushi et al. [7] was able to control the S/(S + Se) ratio to within 0.3, resulting in cell efficiency of 14.28%. Kim et al. [8,9] used this method to accurately control the sulfur content on the surface of the absorber layer, achieving cell efficiency of 14.2%. Huynh et al. [10] used this method to react with a Cu-In-Ga ternary target precursor to produce CIGSSe with a stable chemical composition, high reproducibility, and cell efficiency of 13.4%. Unfortunately, H$_2$Se and H$_2$S gases are toxic, and this two-stage process is complicated. Plam et al. [11,12] performed simultaneous selenization/sulfurization using evaporated Se and S layers with an S/(S + Se) ratio of 0.12, which resulted in cell efficiency of 13%. Mueller et al. [3] employed simultaneous selenization/sulfurization using pre-evaporated layers of Se and S in conjunction with rapid annealing to enable precise control over the sulfur content, which resulted in cell efficiency of 12%. Unfortunately, the above methods require a complex pre-evaporation process followed by annealing. Huang et al. [13] outlined a simultaneous selenization/sulfurization process for use in the fabrication of Cu(In,Ga)(Se,S)$_2$ thin films using a H$_2$S/H$_2$Se/N$_2$ hybrid gas to study the energy gap of Cu(In,Ga)(Se,S)$_2$ thin film. We had presented a simple non-toxic simultaneous selenization/sulfurization process in CZTSe thin film solar cells to varied the S/(S + Se) ratio and observed the effect on the structural properties of the absorber layer. This method increases device efficiency from 5.2% (conventional non-toxic selenization) to 6.3% when S/(S + Se) = 0.55 [14]. This study presents a non-toxic one-stage selenization/sulfurization process to produce CIGS solar cells.

2. Experiment details

In this experiment, Mo back contact (900 nm) was sputtered via direct current magnetron sputtering on soda lime glass (20 × 20 × 1 mm$^3$) in the area. And then prepared a Cu-In-Ga metal precursor of 750 nm by a Cu$_{0.9}$In$_{0.1}$Ga$_{3}$ ternary target. The Cu-In-Ga metal precursors were sputtered at a working pressure of 0.533 Pa and power of 60 W. One-stage simultaneous selenization/sulfurization was subsequently implemented using non-toxic Se and S vapors in the same graphite box within a quartz tube [14] (as shown in Fig. 1). The annealing temperature was maintained at 525 °C for 30 min until the formation of the chalcopyrite CIGSSe absorber was complete. The heating rate was 20 °C/min. Various S/(S + Se) ratio in the absorber layer were conducted by modulating the Se-S weight ratio in the graphite box. The Se-S weight ratio was 0.6% (0.003 g of S/0.5 g of Se), 2% (0.01 g of S/0.5 g of Se), 6% (0.02 g of S/0.3 g of Se), and 10% (0.03 g of S/0.3 g of Se), respectively. The completed absorber layer was coated with a CdS buffer layer (70 nm) via chemical bath deposition, whereupon transparent conductive films of i-ZnO (50 nm) and SnO$_2$:In (ITO) (350 nm) were deposited by sputtering. Finally, an Al front contact (1000 nm) was deposited by sputtering. The structure of the resulting device was as follows: glass/Mo/CIGSSe/CdS/i-ZnO/ITO/Al.

A field-emission scanning electron microscope (FE-SEM, JEOl JSM-6700F) with operating voltage of 15 kV was used to characterize the morphology of the secondary phases layer. X-ray diffraction (XRD, JEOL TF-SEM JSM7000F, CuK$_\alpha$, $\lambda = 1.54052$ Å) with 0-20 scanning, and Raman analysis (Jobin Yvon T64000 at an excitation wavelength of 633 nm) were used to analyze the secondary phases that formed on the surface of the CIGSSe films. Grazing incident XRD (GIXRD) revealed a grazing incidence angle of 0.3°. SIMS (TOF-SIMS IV) was used to investigate the depth profiles of the thin film elements. Extraction voltages were set at 10 and 12.5 keV, respectively. The current of the O$_2$ ions was set to 80 and 120 nA, which impacted the surface of the samples with energies of 5.5 and 8 kV, respectively.

3. Results and discussion

3.1. Effect of S/(S + Se) ratio on composition and morphology

Table 1 lists the EDS results showing the composition of CIGSSe films with various S/(S + Se) ratios. The S content of the CIGSSe film was shown to increase with an increase in the S/(S + Se) ratio. In this study, the CIGSSe samples produced using simultaneous selenization/sulfurization at different S/(S + Se) ratios were identified using the following codes: S0.04, S0.12, S0.22, and S0.48. The Cu/(In + Ga) ratio at the surface decreased with an increase in the S/(S + Se) ratio. The reason for these effects is outlined in the following section using Raman and SIMS analysis.

Fig. 2 presents topographic and cross-section SE images of CIGSSe thin films with various S/(S + Se) ratios. The upper SEM images show the appearance of the thin film surface, whereas the lower images show cross-sections of the thin film. It was observed that S content affected the crystallization quality of CIGSSe as the S/(S + Se) ratio was increased. Larger grains appear on the CIGSSe thin film when the S/(S + Se) ratio was below 0.22. When the S/(S + Se) ratio was increased to 0.48, the higher S content inhibited grain growth, resulting in a large number of smaller grains [15]. When the S/(S + Se) ratio was increased, the thickness of the MoSe$_2$ layer decreased from 510 nm to less than 100 nm. This is a clear indication of the effect that S has on the growth of the Mo(S,Se)$_2$ layer [14,16]. However, cross-section SEM images of CIGSSe with various S/(S + Se) ratios revealed small grains on the bottom of the absorber layer. The fact that they did not fully react resulted in the formation of poorly crystallized CuGaSe$_2$ phase on the bottom of the CIGSSe near the Mo boundary [17,18]. Kim et al. [8] also observed poorly crystallized and unreacted Cu$_x$Ga$_y$ secondary phases at the bottom of the absorber layer. These small grains are analyzed from a structural perspective in the following section.

3.2. Effects of S/(S + Se) ratio on crystal structure

The crystallization quality and texture of samples with different S/(S + Se) ratios was analyzed using 0/20 XRD and 0.3° GIXRD, as shown in Fig. 3(a) and (b). The CIGSSe thin films in Fig. 2(a) presented chalcopyrite phase diffraction peaks (112), (221), (220/204), (312/116), (400) and (316/332) where 2θ = 26.8°, 35.9°, 44.6°, 53°, 65°, and 71.7° [19]. The diffraction peaks were shifted towards a higher angle with an increase in the S/(S + Se) ratio. The lattice constant was also shown to change with the addition of S atoms to the chalcopyrite phase [20]. The lattice constant decreased with an increase in the S/(S + Se) ratio, thereby shifting the chalcopyrite phase XRD diffraction peak toward a higher angle. The full width at half maximum (FWHM) of the main peak of CIGSSe chalcopyrite phases under various S/(S + Se) ratios was calculated to be 0.23, 0.26, 0.29, and 0.3. The FWHM increased with an increase in S content, which is an indication that the CIGSSe crystallization quality tended to worsen. This is consistent with the evidence of SEM images. As shown in Fig. 3(a), the main diffraction peak of CIGSSe phase was observed when the main peak (112) was shifted toward the right at angle of 1.2° [21], as shown in Fig. 3(b). However, no CIGSSe phase diffraction peak was observed in the 0.3° GIXRD analysis. This can be attributed to the deposition of Ga causing
the accumulation of Ga-rich CuGaSe₂ phase at the bottom of CIGSe absorber layer [17,18]. Using θ/2θ XRD, when 2θ = 31°–32° Cu₂–xSe and MoSe₂ diffraction peaks were observed, when 2θ = 31°, the main diffraction peak (200) of Cu₂–xSe secondary phase was observed [19], and when 2θ = 31.7°, we observed the diffraction peak of MoSe₂ phase (100) [22]. The XRD peaks of the two crystal phases are close to one another and may overlap. Furthermore, 0.3° GIXRD was used to analyze the crystalline texture at the surface of CIGSSe thin films with various S/(S + Se) ratios, as shown in Fig. 3(b). All of the samples underwent secondary phase treatment to remove Cu₂–xSe from the surface of the KCN; therefore, the signal from secondary phase Cu₂–xSe should be weak in 0.3° GIXRD analysis. As shown in Fig. 3(a), the intensity of the diffraction peaks of MoSe₂ phase also decreased with an increase in the S/(S + Se) ratio. This is a clear demonstration that S tends to inhibit the growth of MoSe₂. However, the Raman signal of CuInGaSe₂ chalcopyrite was observed only when the S/(S + Se) ratio was increased to 0.12. When the S/(S + Se) ratio was increased to 0.48, the primary texture of the CIGSSe altered. We also observed a significant weakening in the Raman signal of the primary CuInGaSe₂ chalcopyrite phase and a shift in the Raman signal of the CuInS₂ chalcopyrite phase, with OVC respectively appearing at 154 cm⁻¹ and 327 cm⁻¹. This coincided with the appearance of Raman peaks of CuIn₃Se₅ [24,25] and CuIn₅S₈ [25], as well as many Se and Cu₂–xSe secondary phases at 230 cm⁻¹ and 260 cm⁻¹, respectively [19]. An increase in S content led to a significant increase in the Raman signal of CuIn₃S₅ phase, which is indicative of a higher In content at the surface due to the S-rich CIGSSe absorber (Fig. 4). EDS analysis (Table 1) revealed that the Cu content did not vary with the S/(S + Se) ratio, such that the Cu/(In + Ga) ratio at the surface tended to decrease with an increase in the S/(S + Se) ratio.

3.3. SIMS analysis

Fig. 5 presents SIMS analysis of CIGSSe samples with various S/(S + Se) ratios. Fig. 5 shows that the S content in the absorber layer increased with an increase in the S/(S + Se) ratio. The S may have spread slowly from the bottom absorber layer to the surface, resulting in uniform distribution. It is worth noting that the S content of the surface absorber layer was higher than inside the sample when the S/(S + Se) ratio was increased, thereby increasing the surface energy gap and Voc of the modules. This result is similar to our previous CZTSSe study [14].

As shown in Fig. 6, the addition of S may also affect the distribution of Ga and Na. A higher S content may cause the deposition of Na and a
reduction in the total content of Na. Na ions content decrease with the increase of S content on sample surface. In other words, S content is related to in-diffusion of Na ions. It may also cause the deposition of Ga without a reduction in the total Ga content at the bottom, reaching a peak level at S0.48. Fig. 6(a) shows the result of SIMS depth profiles of Ga content with various S/(S + Se) ratios. When S increases in a sample, the uniform distribution of Ga is not shown. This result seems to be different from the study of Kim et al. [6], Kim et al. found a homogeneous through-film Ga composition in Cu(InGa)(SeS)2 films obtained through a simultaneous “H2Se/H2S” reaction of Cu-Ga-In precursor. However, in this study, we did not find similar results from “Se and S vapors” reaction of Cu-Ga-In precursor. The main reason may be hydrogen. Hydrogen may play an important role for homogeneous through-film Ga composition in Cu(InGa)(SeS)2 films during simultaneous selenization and sulfurization process.

In the following, we examine the small grains at the bottom of the CIGSSe film, which were observed in cross-section SEM images (Fig. 1). Kim et al. [8] reported that those small grains may be unreacted Cu9Ga4 secondary phase; however, our θ/2θ XRD results (Fig. 3(a)) indicate that Cu9Ga4 secondary phase appears only when 2θ = 44.05° [8]. We
Fig. 3. (a) 0-2θ XRD and (b) 0.3° GIXRD results from CIGSSe with various S/(S + Se) ratios.

Fig. 4. Raman analysis of CIGSSe with various S/(S + Se) ratios: (a) S0.04, (b) S0.12, (c) S0.22, (d) S0.48.
can therefore deduce that the grains may be CuGaSe$_2$ phase. Mueller and Moon et al. [17,18] reported that the deposition of Ga results in the formation of Ga-rich CuGaSe$_2$ at the bottom of CIGS. CIGS/S element depth profiles (Fig. 4) also reveal Ga deposition within the CIGS/S samples. According to 6/20 XRD analysis (Fig. 2(a)), CuGaSe$_2$ occurred next to CIGS/S thin film main peak (112). Thus, according to cross-section SEM analysis, the grains on the bottom of CIGS/S may be Cu-GaSe$_2$ phase.

In principal, the simultaneous selenization/sulfurization methods employ to CIGS/S (this study) or CZTSSe solar cells [14] with similar benefits. The main benefits include that increase in the surface energy gap of the solar cell and inhibit excessive growth of the Mo(S,Se)$_2$ layer and thereby enhance cell efficiency. The other hand, in the CIGS/S solar cells, we found that a higher S content may cause the deposition of Na and a reduction in the total content of Na. Na ions content decrease with the increase of S content on sample surface. In other words, S content is related to in-diffusion of Na ions. But we did not find this phenomenon in CZTSSe solar cells [14].

3.4. Device efficiency

Fig. 7 presents the J-V curves and device efficiency of samples with various S/(S + Se) ratios. The $J_{SC}$ of CIGS/S devices decreased with an increase in $V_{OC}$ as well as an increase in S content, compared to the devices that underwent discrete selenization and sulfurization. S0.12 presented the highest cell efficiency of 12.8%. Increasing the S content resulted in a higher $V_{OC}$ due to an increase in the total S content in the absorber layer and an increase in the S content at the surface of the absorber layer. Nonetheless, an overly high S content could lead to a decrease in the efficiency of CIGS/S devices. A higher S/(S + Se) ratio led to high defect density deep into the S-rich absorber layer. These defects could promote electron-hole recombination [3,5]. SEM images of the samples (Fig. 1) indicate that S limits the thickness of the MoSe$_2$ layer; however, a degree of thickness may be beneficial to cell efficiency [26–28]. Raman analysis (Fig. 3) revealed Cu$_{2-x}$Se secondary phase in the CIGS/S absorber layer when S content reached S0.48. It is likely that these secondary phases could undermine device efficiency [13]. The highest cell efficiency in this study was achieved when using the two-stage H$_2$Se and H$_2$S process [19,29], thereby demonstrating that the proposed non-toxic process is applicable to CIGS/S surface sulfurization. The highest cell efficiency in this study (12.8%) was obtained when the S/(S + Se) ratio was 0.12. This is close to the efficiency of our previous specimens produced using a two-stage selenization/sulfurization process based on toxic H$_2$Se/H$_2$S gases of 13.1% [19] and 10.2% [29]. Their preparation conditions for the CIGS/S absorber layer were: (1) deposited a Cu$_{0.9}$In$_7$Ga$_3$ ternary target to form a metal precursor by sputtering, (2) conducted a two-stage selenization and sulfurization process, in which H$_2$Se was used for selenization at a holding temperature of 380 °C and soaking time of 10 min followed by sulfurization at a holding temperature of 550 °C with soaking time of 10 min.
Fig. 6. SIMS depth profiles of samples with various $S/(S + Se)$ ratios: (a) Na content and (b) Ga content.
Fig. 7. J–V curves and device efficiency from samples with various S/(S + Se) ratios. The device in this study was produced using non-toxic Se and S gases in a one-stage process.

4. Conclusions

This paper proposes a non-toxic simultaneous selenization/sulfurization process to produce CIGS Se solar cells without the need for the conventional two-stage process using toxic H2Se/H2S gases. Analysis results reveal that the S content of the CIGS Se film increased with an increase in the S/(S + Se) ratio, which caused a decrease in the thickness of the MoSe2 layer from 510 to nm to less than 100 nm. The proposed process was also shown to prevent the peeling of the absorption layer from the substrate following selenization. With an S/(S + Se) ratio ≧ 0.12, the sulfur content on the surface of the absorber layer was higher than inside the samples, which led to an increase in the surface energy gap and Voc of the solar cell. We achieved optimal cell efficiency of 12.8% when the S/(S + Se) ratio was 0.12. This is close to the efficiency of previous specimens produced using a two-stage selenization/sulfurization process based on toxic H2Se/H2S gases of 13.1% and 10.2%. In additional, we mentioned that the non-toxic process only affects the grain growth of the absorber, but also affects the surface energy gap and the distribution of Ga and Na. S content more or less affects the efficiency of the cells made by this method. The content of sulfur not only affects the grain growth of the absorber, but also affects the surface energy gap and the distribution of Ga and Na. S content more or less affects the efficiency of the solar cells.

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