Research Article

The Effect of Ga_2Se_3 Doping Ratios on Structure, Composition, and Electrical Properties of $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ Absorber Formed by Thermal Sintering

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Chalcopyrite compounds of copper indium gallium diselenide (CIGS) absorber were fabricated by using binary-particle (Cu_2Se , In_2Se_3 , and Ga_2Se_3) precursors with thermal sintering method. The binary-particle ink was firstly prepared by milling technology and then printed onto a soda lime glass substrate, which was baked at a low temperature to remove solvents and form a dry precursor. Following milling, the average particle size of agglomerated CIGS powder is smaller than $1.1\ \mu\text{m}$. Crystallographic, stoichiometric, and electrical properties of precursor CIGS films with various doping amounts of Ga_2Se_3 had been widely investigated by using thermal sintering in a nonvacuum environment without selenization. Analytical results reveal that the CIGS absorption layer prepared with a Ga_2Se_3 doping ratio of 3 has a chalcopyrite structure and favorable composition. The mole ratio of $\text{Cu}:\text{In}:\text{Ga}:\text{Se}$ of this sample was $1.03:0.49:0.54:1.94$, and related ratios of $\text{Ga}/(\text{In} + \text{Ga})$ and $\text{Cu}/(\text{In} + \text{Ga})$ were 0.52 and 0.99, respectively. The resistivity and carrier concentration were $3.77\ \text{ohm-cm}$ and $1.15 \times 10^{18}\ \text{cm}^{-3}$.

1. Introduction

Chalcopyrite compounds of copper indium gallium diselenide (CIGS) and related alloys are among the most promising materials for photovoltaic applications [1]. CIGS-based solar cells have potential portable applications because of their high absorption coefficient, large absorption spectrum, and high stability. Recent investigations have revealed efficiencies as high as 20.3% for thin-film CIGS-based solar cells [2].

A set of low-cost approaches with the realistic potential to reduce direct manufacturing costs has been developed in the last five years. Industrial production of CIGS solar cell is mostly based on vacuum processes, which depends on a high initial investment in manufacturing machines. These low-cost techniques typically involve the use of simple and fast nonvacuum deposition methods and the molecular prefixing of the film composition in a precursor layer, which is chemically and thermally treated to form a high-quality CIGS film.

In recent years, CIGS absorbing layers had been fabricated using nanoparticles [3–5] and other coating methods. For nanoparticle-based process, there are two approaches to be used to form the CIGS absorption layer. One is the preparation of a precursor film by synthesizing CIGS powder [3] and the other one is a mechanochemical process (MCP) [4] or a rotary ball milling (RBM) method implemented before nonvacuum coating [5]. For MCP, four elemental metal powders of Cu, In, Ga, and Se are mixed and milled by the planetary ball milling technology, yielding a particle size of $1\ \mu\text{m}$ after milling [4]. For RBM, the precursor has quaternary compound composition ratios of $\text{Cu}/(\text{In} + \text{Ga}) = 0.95$, $\text{Ga}/(\text{In} + \text{Ga}) = 0.39$, and $\text{Se}/(\text{Cu} + \text{In} + \text{Ga}) = 0.75$. After milling, the particle size of the agglomerated CIGS powder is less than $100\ \text{nm}$ [5]. Thus, thermal sintering can cause precursor films forming the dense absorption layer for use in solar cells [6]. All steps performed in a nonvacuum environment are relatively simple and inexpensive, such as ease of scalup [7] and excellent control of the ratios of the metal concentrations. To fabricate low-cost and printable

TABLE 1: Data of CIGS samples sintered at various doping ratios of Ga_2Se_3 .

Parameter	Samples				
	CIS	CIGS-1	CIGS-2	CIGS-3	CIGS-4
$\text{Cu}_2\text{Se} : \text{In}_2\text{Se}_3 : \text{Ga}_2\text{Se}_3$	1 : 5.67 : 0	1 : 5.67 : 1	1 : 5.67 : 2	1 : 5.67 : 3	1 : 5.67 : 4
Cu (at.%)	24.80	30.86	28.32	25.67	21.01
In (at.%)	25.12	16.70	15.44	12.36	10.48
Ga (at.%)	0.00	4.35	7.09	13.56	17.93
Se (at.%)	50.08	48.09	49.15	48.41	50.59
Mole ratio of Cu	0.99	1.23	1.13	1.03	0.84
Mole ratio of In	1.00	0.67	0.62	0.49	0.42
Mole ratio of Ga	0.00	0.17	0.28	0.54	0.72
Mole ratio of Se	2.0	1.92	1.97	1.94	2.02
Ga/(In + Ga)	0.00	0.21	0.31	0.52	0.63
Cu/(In + Ga)	0.99	1.47	1.26	0.99	0.74
Resistivity (ohm-cm)	44.8	0.408	6.89	3.77	41.8
Carrier concentration (cm^{-3})	$2.44 \text{ E} + 15$	$6.25 \text{ E} + 18$	$5.64 \text{ E} + 16$	$1.15 \text{ E} + 18$	$1.66 \text{ E} + 17$
(112) plane	26.575°	26.675°	26.975°	27.075°	27.175°
(220)/(204) plane	44.175°	44.425°	44.725°	44.975°	45.125°
(312)/(116) plane	52.325°	52.575°	53.125°	53.325°	53.525°

CIGS thin-film solar cells, Lee et al. [8] developed a precursor solution by using a nanoparticle-based method in 2011. In that process, a nearly carbon-free CIGS film can be obtained by applying a three-step heat treatment process: the first step is the elimination of carbon residues by air annealing, the second step is the formation of CIGS alloys by sulfurization, and the third step is the grain growth and the densification of CIGS films by selenization.

This work proposes another process to fabricate a CIGS absorption layer by using binary-particle precursors, such as Cu_2Se , In_2Se_3 , and Ga_2Se_3 , through thermal sintering. Crystallographic, stoichiometric, and electrical properties of $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ absorber prepared with binary-particle precursors affected by the doping amount of Ga_2Se_3 were examined and analyzed through various measurements, such as scanning electron microscopy (SEM), X-ray diffractometry (XRD), energy dispersive spectrometry (EDS), Hall measurement, and thermogravimetry analyzer (TGA). Consequently, an optimized doping amount of the Ga_2Se_3 for forming $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_{2.0}$ absorption layers could be obtained.

2. Experiment

Three binary-alloy powders were mixed with appropriate solvents, whose initial stoichiometric ratios are presented in Table 1. Those powders were then ground into binary-alloy particles by using a mill technology to form the ink that was required for preparing the film precursors. Three commercially available binary-alloy powders of In_2Se_3 , Ga_2Se_3 , and Cu_2Se with grain sizes of approximately $74 \mu\text{m}$ (Williams Advanced Materials Technologies Taiwan Co., Ltd., 99.99%) were used as starting materials for forming CIGS absorption layers in a nonvacuum environment.

To obtain the ink for forming CIS and CIGS precursor films, three starting materials were mixed with solvent and

FIGURE 1: SEM photograph. The average grain size of agglomerated CIGS powder after milling is smaller than $1.1 \mu\text{m}$.

zirconium beads; each zirconium bead (diameter: 0.5 mm and mass: 20 g) was ground continuously in a mill for eight hours to produce the required ink. The SEM photograph shows that the average grain size of agglomerated CIGS powders is less than $1.1 \mu\text{m}$, as shown in Figure 1. After the ink printed onto a soda lime glass substrate, the solvent was removed by placing the sample into an oven at a temperature of 120°C and maintaining for 5 min. Then, the temperature was increased from 120 to 200°C at the same rate and maintained at 200°C for 10 min. Once the oven turned off, the expected dry precursor film could be obtained when the sample was cooled down to the room temperature. Subsequently, the $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_{2.0}$ absorption layer for use in solar cells can be formed by thermal sintering.

The weight loss of Cu_2Se , In_2Se_3 , and Ga_2Se_3 measured by TGA is as shown in Figure 2. The data shows that the loss of Cu_2Se is 2% at 520°C , whereas the losses of In_2Se_3 and Ga_2Se_3 are 32.5% and 25%, respectively, at 420°C . Based on these data, the sintering temperature was set at

FIGURE 2: TGA data for weight losses of Cu_2Se , In_2Se_3 , and Ga_2Se_3 .

420°C and maintained for 30 min; then the temperature was increasing from 420 to 520°C and maintained at 520°C for one hour. Subsequently, prepared precursor samples were heated in a thermal annealing furnace filled with nitrogen. Thus, $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_{2.0}$ films with highly uniform crystalline structure could be formed. After one hour, the temperature was dropped below 50°C. Since the amount of Ga_2Se_3 can affect the film structure of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_{2.0}$ sample, the properties of the sample can be analyzed according to this point.

3. Results and Discussion

3.1. Structural Properties. Figure 3 presents the XRD patterns of samples that were sintered with various amounts of Ga_2Se_3 . The XRD measurement was executed by scanning the diffraction angle from 20 to 60° and using a grazing incidence angle of 1°. In Figure 3, XRD patterns display that sintered CIGS samples have many diffraction peaks at (112), (220)/(204), and (312)/(116), corresponding to different crystalline structures, respectively.

From sample CIS to sample CIGS-4, the XRD peak at (112) shifts from 2-theta = 26.575° to 2-theta = 27.175°. According to the results reported by Balboul et al. [9], the compositions were determined by calculating the peak shift with the ratio of In : Ga. As Ga content increases, the doublet of peaks, that is, (220)/(204) peak and (116)/(312) peak, is splitting into two individual parts. This splitting indicates that the deviation of tetragonality, that is, $c/a = 2$, was resulted by Ga substitution. These results are ascribed to the small ionic size of Ga, 0.62 Å, compared to that of In, 0.81 Å. As Ga_2Se_3 ratio increases, all signals shift towards larger diffraction angles. Figure 3 shows this effect on the signal of (112). This noticeable shift is due to the decrease in lattice constants “a” and “c” as reported by Olejník et al. [10]. The chalcopyrite structure of $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_{2.0}$ was modeled using the space

FIGURE 3: XRD patterns of sintered samples with various doping amounts of Ga_2Se_3 .

group I42d (122) with standard lattice constants of $a = 5.673$ Å and $c = 11.322$ Å (JCPDS-40-1488) [11, 12]. Table 1 and Figure 3 reveal that the 2-theta data of the sintered sample with a Ga_2Se_3 doping ratio of 3 (CIGS-3) are very close to those on the JCPDS card (40-1488) for $\text{Cu}(\text{Ga}_{0.5}\text{In}_{0.5})\text{Se}_{2.0}$ at the angles of 27.075°, 44.975°, and 53.325°, respectively.

3.2. Compositions. The stoichiometric compositions of CIGS samples having various Ga_2Se_3 doping ratios were analyzed by using EDS data, as shown in Table 1. An attempt was also made to optimize the Cu, In, Ga, and Se contents in the CIGS absorption layer of solar cells. The $\text{Ga}/(\text{In} + \text{Ga})$ and $\text{Cu}/(\text{In} + \text{Ga})$ mole ratios presented in Table 1 were obtained by using various Ga_2Se_3 doping ratios. For samples sintered with various Ga_2Se_3 doping ratios, their ratios of $\text{Ga}/(\text{In} + \text{Ga})$ and $\text{Cu}/(\text{In} + \text{Ga})$ are shown in Figure 4. Since the mole ratios of $\text{Ga}/(\text{In} + \text{Ga})$ and $\text{Cu}/(\text{In} + \text{Ga})$, respectively, are 0.52 and 0.99, the doping ratio of Ga_2Se_3 for CIGS-3 sample is the optimal. For this sample, its doping ratio of Ga_2Se_3 is 3. This reveals that the Cu : In : Ga : Se mole ratio of CIGS-3 is 1.03 : 0.49 : 0.54 : 1.94, which is approximately 1 : 0.5 : 0.5 : 2.0 reported elsewhere [13]. For fixed Cu content, the $\text{Ga}/(\text{In} + \text{Ga})$ ratio and the 2-theta at (112)-peak of each sintered sample corresponding to various Ga_2Se_3 doping ratios are shown in Figure 5. Furthermore, the main XRD peaks (112) shown in Figure 3 display a noticeable shift that the higher the angle, the larger the doping ratio of Ga_2Se_3 , which has also been reported elsewhere [14–17]. This is attributed to relatively small Ga atoms substituting for larger In atoms in the chalcopyrite structure [17], resulting in a decrease in the lattice parameter.

3.3. Electrical Properties. Parameters related to electrical, structural, and compositional properties of each CIGS sample

FIGURE 4: Ga/(In + Ga) and Cu/(In + Ga) ratios of each sintered sample.

FIGURE 6: The resistivity and carrier concentration of each sintered sample.

FIGURE 5: The Ga/(In + Ga) ratio and the 2-theta at (112)-peak of each sintered sample corresponded to various Ga₂Se₃ doping ratios.

FIGURE 7: The Cu/(In + Ga) and Ga/(In + Ga) ratios and resistivity of each sintered sample.

are listed in Table 1. The carrier concentration and the electrical resistivity of all sintered CIGS samples were determined by Hall measurement [18], as shown in Figure 6. Measuring data shows that all samples are p-type. At room temperature, each sample has an electrical resistivity between 0.408 and 44.8 ohm-cm and an associated carrier concentration from 2.44×10^{15} to $6.25 \times 10^{18} \text{ cm}^{-3}$. The CIGS-1 sample has the lowest resistivity of 0.408 ohm-cm and the highest carrier concentration of $6.25 \times 10^{18} \text{ cm}^{-3}$. The CIS sample has the highest resistivity of 44.8 ohm-cm and the lowest carrier concentration of $2.44 \times 10^{15} \text{ cm}^{-3}$. For specified Ga content, Figures 7 and 8, respectively, show the ratios of Cu/(In + Ga) and Ga/(In + Ga) of each sintered sample and their related resistivity and carrier concentration. These two figures reveal that CIGS-1 had the highest ratio of Cu/(In + Ga), the lowest resistivity of 0.408 ohm-cm, and the highest carrier concentration of $6.25 \times 10^{18} \text{ cm}^{-3}$. Sample CIGS-4 has a lower

ratio of Cu/(In + Ga) and a higher ratio of Ga/(In + Ga), as well as the highest resistivity of 41.8 ohm-cm and a carrier concentration of $1.66 \times 10^{17} \text{ cm}^{-3}$. For sample CIGS-3, however, its resistivity and carrier concentration are 3.77 ohm-cm and $1.15 \times 10^{18} \text{ cm}^{-3}$, respectively. Moreover, according to the pieces of literature reported by Turcu and Rau and Zhang et al. [19, 20], the Cu-rich films phase has lower electrical resistivity and higher carrier concentration, whereas the Cu-poor films phase has higher electrical resistivity and lower carrier concentration.

Based on the data shown in Section 3.2, the ratio of Cu/(In + Ga) of the sample CIGS-3 is nearly equal to one, so that it is very suitable for the $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_{2.0}$ absorbing layer having the required resistivity and carrier concentration [21–26]. For this sample, the ratios of Cu/(In + Ga) = 0.99 and Ga/(In + Ga) = 0.52 were optimal because the mole ratio of Cu:In:Ga:Se is very close to the expected value

FIGURE 8: The Cu/(In + Ga) and Ga/(In + Ga) ratios and carrier concentration of each sintered sample.

of 1:0.5:0.5:2.0 [13]. At the same time, the 2-theta data of CIGS-3 is also close to that on the JCPDS card (40-1488) for $\text{Cu}(\text{Ga}_{0.5}\text{In}_{0.5})\text{Se}_{2.0}$. Additionally, the data of 2-theta at the peak of (112) increases with the doping amount of Ga_2Se_3 . This is consistent with the result reported by other several works [14–17].

4. Conclusions

In this paper, a CIGS absorber prepared by using binary-particle (Cu_2Se , In_2Se_3 , Ga_2Se_3) precursors via thermal sintering method had widely been investigated. The required binary-particle ink for fabricating the absorbing layer was prepared by using the milling technology. The SEM photograph reveals that the average particle size of the agglomerated CIGS powder is smaller than $1.1\ \mu\text{m}$ after milling. Analytical results obtained from measurements of SEM, XRD, EDS, Hall, and TGA reveal that the CIGS-3 sample has a chalcopyrite structure and a favorable composition of $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_{2.0}$. The Cu : In : Ga : Se mole ratio of CIGS-3 is 1.03 : 0.49 : 0.54 : 1.94, and its resistivity and carrier concentration are $3.77\ \text{ohm-cm}$ and $1.15\ \text{E} + 18\ \text{cm}^{-3}$, respectively. Among those sintered samples prepared in our laboratory, the 2-theta data of CIGS-3 is very close to the data on the JCPDS card (40-1488) for $\text{Cu}(\text{Ga}_{0.5}\text{In}_{0.5})\text{Se}_{2.0}$. In summary, our investigations mainly focused on crystallographic, stoichiometric, and electrical properties of $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_{2.0}$ thin film and obtained the optimized doping amount of Ga_2Se_3 in a CIGS absorbing layer.

Conflict of Interests

All authors declare that there is no conflict of interests regarding the publication of this paper.

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