

Effect of Soft-annealing on the Properties of CIGSe Thin Films Prepared from Solution Precursors

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Solution-based deposition of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGSe) thin films is well known non-vacuum process for the fabrication of CIGSe solar cells. However, due to the usage of organic chemicals in the preparation of CIG precursor solutions, the crystallization of the polycrystalline CIGSe and the performance of CIGSe thin film solar cells were significantly affected by the carbon residues from the organic chemicals. In this work, we have tried to eliminate the carbon residues in the CIG precursor thin films efficiently by using soft-annealing process. By adjusting soft-annealing temperature, it is possible to control the amount of carbon residues in CIG precursor thin films. The reduction of the carbon residues in CIG precursors by high temperature soft-annealing improves the grain size and morphology of polycrystalline CIGSe thin films, which are also closely related with the electrical properties of CIGSe thin film solar cells.

Key Words : CIGSe, Thin film, Solar cell, Solution deposition, Carbon residue

Introduction

Due to high absorption coefficient and optimum band gap energy, solar cells based on polycrystalline $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGSe) thin films have proven to be a promising candidate for industrial applications.^{1,2} Nowadays, vacuum based processes, such as sputtering and co-evaporation, are well established for the deposition of CIGSe absorber layers with high efficiency, but high cost and low material utilization of the vacuum equipment seems to be the obstacle to the commercialization of CIGSe solar cells. In order to overcome the drawbacks of the vacuum process, alternative non-vacuum processes for the preparation of CIGSe thin films, such as direct liquid coating,^{3,4} spin coating,^{5,6} and paste coating,⁷ have been widely investigated. Solution-based deposition methods are simple processes, suitable for large-area, and high-throughput manufacturing.

Among various solution-based deposition methods such as the synthesis of CIGSe nanoparticle,⁸⁻¹⁰ and the use of hydrazine-based CIGSe solution,⁹ and selenization of CIG precursors,^{12,13} the selenization of CIG precursors has attracted much attention because it is a simple and non-toxic method. However, the selenization of CIG precursors requires the usage of organic chemicals in the preparation of CIG precursors requisitely in order to acquire good quality thin film. However, the carbon residues from these organic chemicals have negative effects on the crystallization of the CIG precursors such as poor crystal growth and impurities in crystalline structures, which diminish the performance of CIGSe solar cells considerably.

In this work, we have investigated the effect of carbon residues on the crystallization behavior and current-voltage characteristics of CIGSe thin films and tried to eliminate the carbon residues in the precursor thin films efficiently by

using soft-annealing process. By adjusting the temperature of soft-annealing process, it was possible to control the amount of carbon residues in CIG precursor thin films. The carbon residues in the precursors were closely related with the morphology and crystalline structure of CIGSe thin films and the photovoltaic performances of CIGSe thin film solar cells.

Experimental

Preparation of CIGSe Thin Films. CIG precursor thin films were layered onto molybdenum-coated soda lime glass substrates. The substrates were ultrasonically cleaned with acetone, then methanol, and finally rinsed with de-ionized (DI) water for 10 min, respectively. They were dried with nitrogen gas before being used for the deposition process. A precursor solution for the CIG layer was prepared by dissolving 0.6 M of Cu(II) acetate, 0.42 M of In(III) acetate, and 0.18 M of Ga(III) acetylacetonate in 20 mL of 2-methoxyethanol. The ethanolamine was used as stabilizer. The stoichiometric ratio of the Cu:In:Ga was 1:0.7:0.3.

To prevent the inflow of O_2 in CIG precursor, a deposition process of the CIG precursor was performed in a nitrogen-filled glove box with water and O_2 levels maintained below 1 ppm. The CIG precursor thin films were deposited by a spin-coating method. The prepared solution was passed through a 0.2 μm filter and spin-coated at 3000 rpm for 10 s. The spin-coated precursor thin films were treated by soft-annealing process at 150, 250, and 350 $^\circ\text{C}$ for 3 min on a hotplate in a nitrogen-filled glove box.

In order to convert the CIG precursor into CIGSe, prepared CIG precursor thin film was followed by the 2-step selenization process. In the 1st step of selenization process, temperature was maintained at 250 $^\circ\text{C}$ for 60 min to in-

corporate sufficient Se onto the CIG precursors. In the 2nd step selenization process, the temperature was maintained at 600 °C for 60 min to obtain good crystallinity and grain growth. The Se vapor was provided onto the CIG precursor films by evaporation at a deposition rate of 10 Å/s.

Characterization of CIGSe Thin Films. Thermal gravimetric analysis (TGA) was conducted using SDT Q600 (TA Instruments) in nitrogen atmosphere. The chemical composition of the CIG and CIGSe thin films was measured via energy dispersive x-ray spectrometer (EDS) analysis. The surface morphology and grain growth of the prepared films were investigated with a scanning electron microscope (SEM, Hitachi S-4800). The crystal structure and crystallographic orientation of the CIGSe thin films were identified by an analysis with an x-ray diffraction spectrometer (XRD, Panalytical MPD for thin film).

Fabrication of Characterization of CIGSe Solar Cells. A CdS (buffer layer) was deposited on the CIGSe thin films by using a chemical bath deposition (CBD) method. Subsequently, intrinsic-zinc oxide (*i*-ZnO) and aluminium zinc Oxide (AZO) window layers were deposited by radio frequency-sputtering process. Finally, an aluminium (Al) electrode as the front contact was deposited by using a thermal evaporator. The electrical properties of completed CIGSe thin film solar cells were investigated by measuring current-voltage characteristic under simulated AM 1.5 solar irradiation and standard test conditions.

Results and Discussion

The selenization of CIG precursors is one of the cost-effective preparation methods of CIGSe thin films for solar cells. In order to form high quality CIGSe thin films, CIG precursor thin films with sufficient thickness and good uniformity are required. For good thin film formability, various organic materials such as binders or stabilizer should be added into the precursor solution inevitably. However, these organic materials could remain in the CIGSe thin films after selenization process and they have a significant effect on the crystalline properties of CIGSe thin films. To overcome the side effect of the organic materials in CIG precursor thin films, an efficient elimination method of the organic materials must be considered. In our work, we have applied a soft-annealing treatment of CIG precursor thin films before selenization process. In order to study the effect of the soft-annealing on the CIG precursor properties, weight loss of CIG precursor thin films according to the temperature of soft annealing was firstly observed.

Figure 1 shows TGA curves of powders scraped from CIG precursor thin films with different soft-annealing temperature. CIG precursor with 150 °C has three regions of weight loss in the TGA curve, 90-150, 150-210 and 210-400 °C. Weight loss in 90-150 and 150-210 °C region is resulted from the evaporation of solvent, 2-methoxymethanol (b.p. = 125 °C) and stabilizer, ethanolamine (b.p. = 170 °C), respectively. In 210-400 °C region, metal sources such as Cu(II) acetate, In(III) acetate, and Ga(III) acetylacetonate in precursor de-

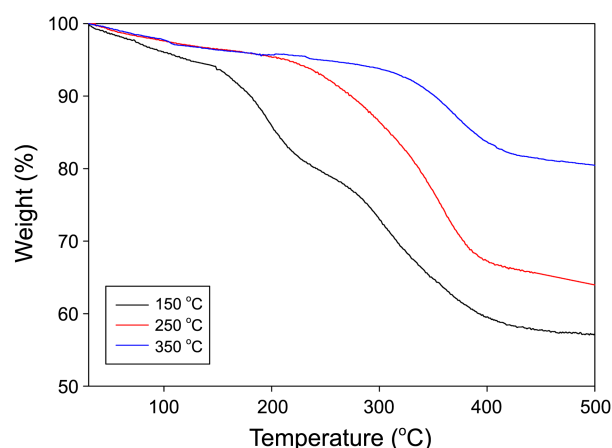


Figure 1. TGA of CIG precursor thin films as a function of soft-annealing temperature; 150, 250, 350 °C.

Table 1. Weight ratio of carbon and metal elements in CIG precursor thin films with different soft-annealing temperature; 150, 250, 350 °C

Weight Ratio (wt %)	Soft-annealing Temperature		
	150 °C	250 °C	350 °C
Cu+In+Ga	12.57	35.36	36.23
C	28.16	24.29	20.01
C/(Cu+In+Ga)	2.24	0.69	0.55
Cu/In	0.67	0.66	0.91
Cu/Ga	2.62	2.97	2.96

compose and the weight loss of carbon and oxygen elements occurs. In the case of 150 °C soft-annealing, three regions of weight loss are evident, which means that CIG precursor thin film contains all of solvent, stabilizer, and metal sources. On the other hand, CIG precursors with 250 °C and 350 °C soft-annealing show slight weight loss around 210 °C and weight loss of 350 °C soft-annealing is smaller than that of 210 °C. This result reveals that the temperature of soft-annealing is closely related with the amount of carbon residues in CIG precursor thin films.

In order to clarify the effect of soft-annealing temperature on the amount of carbon residues in CIG precursor thin films, weight composition of CIG precursor thin films with different soft-annealing temperature was investigated by using EDS analysis (Table 1).

As soft-annealing temperature increased, the weight fraction of metal and carbon elements increased and decreased respectively, and as a result, the relative ratio of carbon to metal elements in CIG precursor thin films decreased. This result means that elimination of carbon residues in CIG precursor thin films is closely related with the soft-annealing process. From TGA data, it was supposed that the elimination of organic materials in the CIG precursor was accelerated by increasing the soft-annealing temperature. Besides carbon residues, relative fraction of metals in CIG precursor thin films was also affected by the temperature of soft-annealing temperature. While Cu/In weight ratio increased

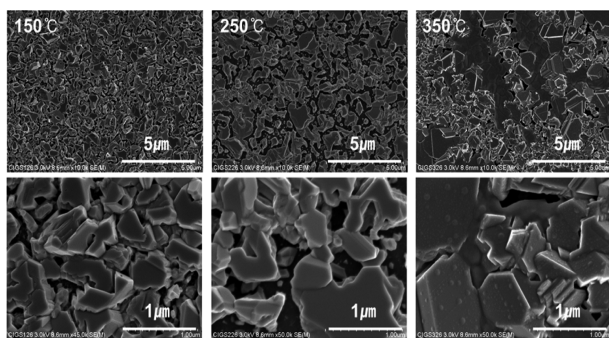


Figure 2. SEM images of CIGSe thin films after selenization process as a function of soft-annealing temperature; 150, 250, 350 °C.

from 0.67 to 0.91 by 350 °C soft-annealing, Cu/Ga weight ratio increased from 2.67 to 2.97 just by 250 °C soft-annealing process. This result would be closely related with the volatility of the metal compounds in CIG precursor thin films. Due to higher volatility of Ga compound, weight fraction of Ga might be easily decreased just by 250 °C. Unlike Ga, relative fraction of In in CIG precursor thin films was affected by 350 °C soft-annealing because of lower volatility of In compound compared with Ga. From TGA and EDS analysis of CIG precursor thin films, it could be concluded that soft-annealing of CIG precursor thin films at higher temperature is effective method for controlling the carbon residues in CIG precursor thin films.

Carbon residues in CIG precursors are known to have a significant effect on the crystallization behavior of the CIG precursors.^{14,15} In order to investigate the effect of carbon residue in CIG precursor thin films on the formation of polycrystalline CIGSe thin film, surface morphology of the CIGSe thin films after selenization process with different soft-annealing temperature was observed by using SEM (Figure 2).

As soft-annealing temperature increases, the grain size of polycrystalline CIGSe increases and the surface morphology of CIGSe thin films improved. The improved grain size and morphology of polycrystalline CIGSe thin films might be closely related with the amount of carbon residue in CIG precursor thin films. The carbon residues in the CIG precursor act as impurity in the procedure of crystallization of polycrystalline CIGSe. Therefore, in the case of CIGSe thin films with 150 °C soft-annealing, grain growth of polycrystalline CIGSe is easily disturbed by the carbon residue and thus the grain size of CIGSe polycrystalline is small and the morphology is sparse. However, on contrary to 150 °C soft-annealing, CIGSe thin films with 350 °C soft-annealing shows larger grain size (over 1 μm) of polycrystalline CIGSe and dense morphology of CIGSe thin films. This result might be attributed to the smaller amount of carbon residues in CIG precursor thin films with 350 °C soft-annealing, which was confirmed by TGA and EDS results. From these results, it was found that efficient elimination of carbon residues in the CIG precursor thin films is indispensable for converting CIG precursor thin films to high quality CIGSe thin films.

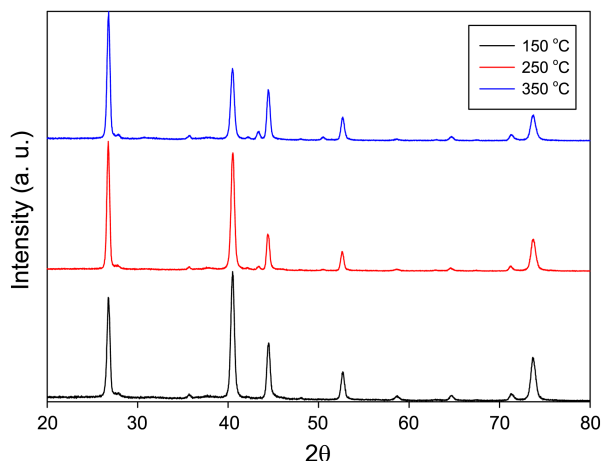


Figure 3. XRD pattern of CIGSe thin films after selenization process as a function of soft-annealing temperature; 150, 250, 350 °C.

For the confirmation of polycrystalline structure of CIGSe, XRD pattern of CIGSe thin films with different soft-annealing temperature was obtained (Figure 3). All the samples show a typical XRD pattern of CIGSe. It was found that the diffraction peaks closely match the values of standard data (JCPDS No.00-035-1102) and can be indexed as $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ with tetragonal structure. In addition, there was no XRD peak of other second phase in CIGSe thin films. From these results, it was found that soft-annealing temperature of CIG precursor thin films has little effect on the polycrystalline structure of CIGSe thin films after selenization process.

Finally, in order to elucidate the correlation between carbon residues in CIG precursor thin films and actual solar cell performance of CIGSe thin film solar cells, solar cell devices were constructed using the CIGSe thin films with different soft-annealing temperatures. The CIGSe thin film solar cells were fabricated with the configuration of Mo/CIGSe/CdS/ZnO/AZO/Al.

As shown in Figure 4, the current density-voltage (J-V) characteristics of the solar cells revealed that CIGSe thin

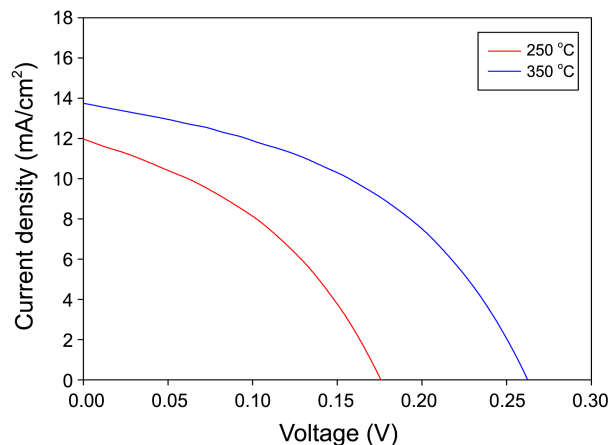


Figure 4. I-V graph of CIGSe solar cells with different soft-annealing temperature; 250 and 350 °C. CIGSe thin film with 150 °C soft-annealing showed no PV characteristics.

Table 2. Electrical properties of CIGSe thin film solar cells with different soft-annealing temperature; 250, 350 °C

Soft-annealing Temperature (°C)	Efficiency (%)	Fill Factor	V_{oc} (V)	J_{sc} (mA/cm ²)
250	0.82	38.94	0.18	11.97
350	1.59	44.21	0.26	13.75

films with higher soft-annealing temperature showed better solar cell performance. Table 2 shows the electrical properties of CIGSe thin film solar cells with different soft-annealing temperature. CIGSe solar cell with 350 °C soft-annealing showed higher efficiency than 250 °C and other properties are also improved by increasing soft-annealing temperature. CIGSe solar cell with 150 °C soft-annealing showed no PV characteristics, which might be attributed to the poor crystalline structure of the CIGSe thin films. From this result, it was found that soft-annealing temperature of CIG precursor thin films had a significant effect on the electrical properties and solar cell performance of CIGSe thin films.

Conclusion

The effect of soft-annealing of CIG precursor thin films prepared by solution-based deposition was investigated. By adjusting the temperature of soft-annealing process, it was possible to control the amount of carbon residues in CIG precursor thin films. As soft-annealing temperature increases, volatile carbon materials are effectively eliminated from the CIG precursor thin films and the relative amount of carbon residues in CIG precursor thin films decreased. Due to the decrease of carbon residues in CIG precursor thin films, the formation of polycrystalline CIGSe by selenization process are less hindered and thus, the grain growth and surface morphology of CIGSe thin films were improved by higher temperature soft-annealing process. It was also found that the current-voltage characteristics of CIGSe thin film solar cells are considerably affected by soft-annealing temperature of CIG precursors. Because of better grain growth of polycrystalline CIGSe, CIGSe thin films with higher soft-annealing temperature showed better electrical properties com-

pared that with lower soft-annealing temperature. From these results, it was found that the soft-annealing process is a crucial factor for control of carbon residues in CIG precursors, which are closely related with the formation of polycrystalline CIGSe and the photovoltaic performances of CIGSe thin films.

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References

1. Lee, D. W.; Choi, Y. W.; Yong, K. J. *J. Cryst. Growth* **2010**, *312*, 3665.
2. Liu, Y.; Kong, D.; You, H.; Zhao, C.; Li, J.; Brugger, J. *Solid State Lett.* **2012**, *1*, 26.
3. Park, M. G.; Ahn, S. J.; Yun, J. H.; Gwak, J. H.; Cho, A.; Ahn, S. K.; Shin, K. S.; Nam, D. H.; Cheong, H. S.; Yoon, K. Y. *J. All. Comp.* **2012**, *513*, 68.
4. Chang, J.; Han, J. E.; Jung, D. Y. *Bull. Korean Chem. Soc.* **2011**, *32*, 434.
5. Oliveira, L.; Todorov, T.; Chassaing, E.; Lincot, D.; Carda, J.; Escibano, P. *Thin Solid Films* **2009**, *517*, 2272.
6. Lee, S. Y.; Park, B. O. *Thin Solid Films* **2008**, *516*, 3862.
7. Park, J. W.; Choi, Y. W.; Lee, E. J.; Yoon, S. H.; Min, B. K. *J. Cryst. Growth* **2009**, *311*, 2621.
8. Tang, J.; Hinds, S.; Kelley, S. O.; Sargent, E. H. *Chem. Mater.* **2008**, *20*, 6906.
9. Liu, W. L.; Wu, M. Q.; Zhou, R. C.; Yan, L. D.; Zhang, S. R.; Zhang, Q. Y. *Bull. Korean Chem. Soc.* **2011**, *32*, 4332.
10. Chung, J.; Kim, S. J. *Bull. Korean Chem. Soc.* **2010**, *31*, 2695.
11. Mitzi, D. B.; Yuan, M.; Liu, W.; Kellock, A. J.; Chey, S. J.; Gignac, L.; Schrott, A. G. *Thin Solid Films* **2009**, *517*, 2158.
12. Park, S. J.; Lee, E.; Jeon, H. S.; Gwak, J.; Oh, M. K.; Min, B. K. *Thin Solid Films* **2012**, *520*, 3048.
13. Jiang, F.; Feng, J. *Thin Solid Films* **2006**, *515*, 1950.
14. Uhl, A. R.; Romanyuk, Y. E.; Tiwari, A. N. *Thin Solid Films* **2011**, *519*, 7259.
15. Lee, E.; Park, S. J.; Cho, J. W.; Gwak, J.; Oh, M. K.; Min, B. K. *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 2928.