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ScienceDirect

Ceramics International 38S (2012) S521–S523

CERAMICS INTERNATIONAL

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Phase analysis of $Cu(In_{1-x}Ga_x)Se_2$ prepared by solvothermal method

Sin-il Gu [a,b], Seung-hyuk Hong [a,b], Hyo-soon Shin [a,*], Youn-woo Hong [a],
Dong-hun Yeo [a], Jong-hee Kim [a], Sahn Nahm [b]

[a] IT Convergence Ceramic Div., Korea Institute of Ceramic Engineering Technology, Seoul 153-801, Republic of Korea
[b] Department of Materials Science and Engineering, Korea University, Seoul 136-701, Republic of Korea

Abstract

For screen printing of $Cu(In_{1-x}Ga_x)Se_2$ (CIGS) in solar cell application, the synthesis of CIGS powder was examined. The solvothermal method was adopted for CIGS synthesis, as it is known that the method could control particle characteristics easily and produce much amount of powders. The phase change and particle shapes were observed with variation of reaction temperature and time. At low reaction temperature of 210 °C, $CuInSe_2$ (CIS) and $CuGaSe_2$ (CGS) were formed first without CIGS. As reaction temperature increased, CIGS phases of different compositions appeared at 230 °C, but made into one stoichiometric composition at 250 °C. With increase of reaction time at 250 °C, the phase ratio did not change significantly and three phases coexisted.

Keywords: A. Powders: chemical preparation; B. X-ray methods; $Cu(In_{1-x}Ga_x)Se_2$; Solar cell

1. Introduction

Solar cell has been focused on recently as prospective new energy resource with predicted exhaustion of fossil fuels [1,2]. And single crystalline solar cell by thin film process has been widely studied. Single crystalline solar cell, however, has been known to have two major disadvantages of low photoelectric conversion rate and expensive cost of single crystalline silicon wafer [3]. To overcome these, some researchers have examined the II–IV compound semiconductor solar cell [4,5]. Among those, $CuIn_{1-x}Ga_xSe_2$ (CIGS) system has been known to have some advantages such as non-toxicity, long time stability, and high conversion efficiency [6]. CIGS has also been examined mostly by thin film process. Though thin film process has been widely adopted, it is known to cost too much due to co-evaporation in vacuum. It can be easily assumed that the process cost could be lowered by non-vacuum thick film process such as screen printing, though nano-sized powder of CIGS is needed for the paste. For the synthesis of nano-sized CIGS powder, the solvothermal method has been mainly adopted, for it could easily control particle characteristics, and produce much amount of powder. But CIGS powder of single phase has never been synthesized by the solvothermal method [7,8]. As similar crystalline phases during synthesis such as $CuInSe_2$ (CIS) and $CuGaSe_2$ (CGS) have been formed and coexisted with CIGS, X-ray diffraction patterns of synthesized mixture could hardly been analyzed. A few researchers have reported the X-ray diffraction patterns of the synthesized mixtures [9].

In this study, nano-sized CIGS powder was synthesized by the solvothermal method. Phase change during process has been observed to examine the effect of reaction temperature and time on phase formation. And the feasibility of single phase CIGS by control of reaction temperature and time has been checked.

2. Experimental procedure

$CuCl_2\cdot 2H_2O$ (99.99%, Junsei Chemical Co. Ltd., Japan), $InCl_3$ (97%, Sigma–Aldrich Co. Ltd., Japan), $GaCl_3$ (99.99%, Sigma–Aldrich Co. Ltd., Japan) and Se (99.99%, Sigma–Aldrich Co. Ltd., Japan) were used as raw materials. And ethylenediamine (99.9%, Sigma–Aldrich Co. Ltd., Japan) was used as solvent.

In the glove box which is filled with mixed gas of Ar (g) and N_2 (g), 0.050 mmol (0.221 g) of $CuCl_2\cdot H_2O$, 0.025 mmol (0.190 g) of $InCl_3$, 0.025 mmol (0.114 g) of $GaCl_3$ and 0.100 mmol (0.205 g) of Se were loaded into the autoclave

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* Corresponding author. Tel.: +82 2 3282 2499; fax: +82 2 3282 7837.
E-mail address: hshin@kicet.re.kr (H.-s. Shin).

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doi:10.1016/j.ceramint.2011.05.067

vessel, which were filled with 43 cm^3 of anhydrous ethylenediamine afterward. The reaction temperature was varied from 190 °C to 250 °C and the reaction time was varied from 8 h to 40 h. The synthesized powders were washed with distilled water to remove chlorine ions and then dried at 100 °C for 24 h.

X-ray diffraction (XRD hereafter) patterns of synthesized powders were observed by X-ray diffractometer (X'pert pro, PANalytical, Netherlands) with use of Cu Kα radiation at scanning speed of 5°/min between $20^\circ < 2\theta < 70^\circ$ at 1200 W (40 kV × 30 mA). The XRD patterns were analyzed with computer-aided phase analysis program (X'pert HighScore Pro, PANalytical, Netherlands) to compare phase ratio. Particle shapes were observed by field emission scanning electron microscope (LSM-6700F, Jeol, Japan) at an accelerating voltage of 20 kV. The ratio of phase was calculated using phase analysis program (X'pert HighScore pro, PANalytical, Netherlands).

3. Results and discussion

Fig. 1 shows XRD patterns of synthesized powders with variation of reaction temperature. At 190 °C, any peak of CIS, CGS, and CIGS could be found but several unknown peaks. The unknown ones were hard to be identified, because intensities of them were too low to be separated and analyzed. At 210 °C of reaction temperature, clear peaks of CIS and CGS appeared respectively. In the cases of 230 °C and 250 °C, peaks of CIS and CGS at (2 0 4) plane were not separated clearly as if another peak coexists between them, and those peaks could be assumed at (1 1 2) plane and (3 1 2) plane. The crystal structures of CIS, CGS, and CIGS are known to be same and make complete solid solution [10]. The broad peak at each plane was thought to indicate coexistence of those three phases. For phase comparison, peaks of (2 0 4) plane were separated and analyzed instead of (3 1 2) plane, due to too low intensities of (3 1 2) plane.

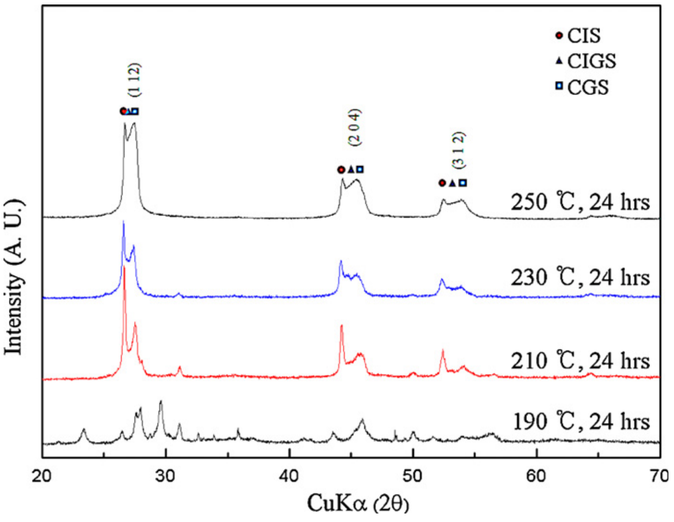

Fig. 1. X-ray diffraction patterns of synthesized powders with reaction temperature.

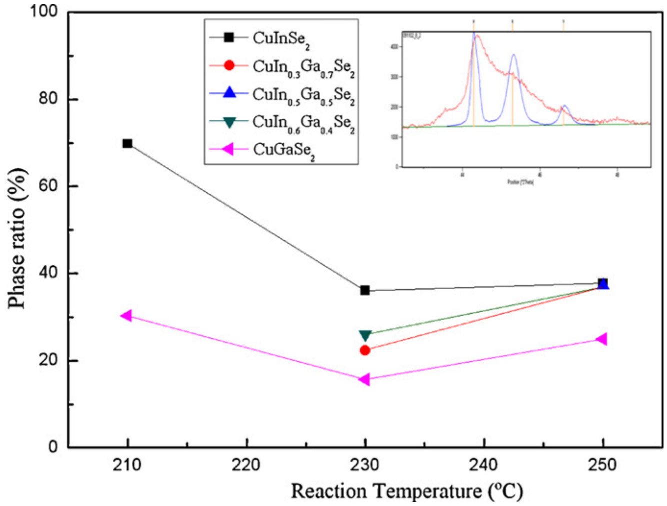

Fig. 2. Phase ratios of CIS, CIGS, and CGS with reaction temperature and calculation of synthesized CIGS.

Fig. 2 shows phase ratios of CIS, CGS, and CIGS calculated from the XRD patterns with variation of reaction temperature. For accurate phase analysis from XRD patterns, Rietveld method has been widely adopted. But for this method, it is known that the peaks must be narrow and separated. As shown in Fig. 1, XRD patterns obtained in this study shows broad peaks which could be hardly separated. So Rietveld method is hard to be adopted in this study. Instead of Rietveld method, despite its insufficient accuracy, peak separation method in X'pert HighScore program was used to calculate the phase ratio. Peaks at (2 0 4) plane was used as mentioned above. As shown in Fig. 1, CIS and CGS appeared at 210 °C and two different CIGS phases were identified at 230 °C. The compositions of two CIGS were identified as $CuIn_{0.3}Ga_{0.7}Se_2$ and $CuIn_{0.6}Ga_{0.4}Se_2$, respectively. The composition was determined from calculation of peak shift along In:Ga ratio and corresponds with the result reported by Balboul et al. [11] who had formed thin film phases by CVD method. And the

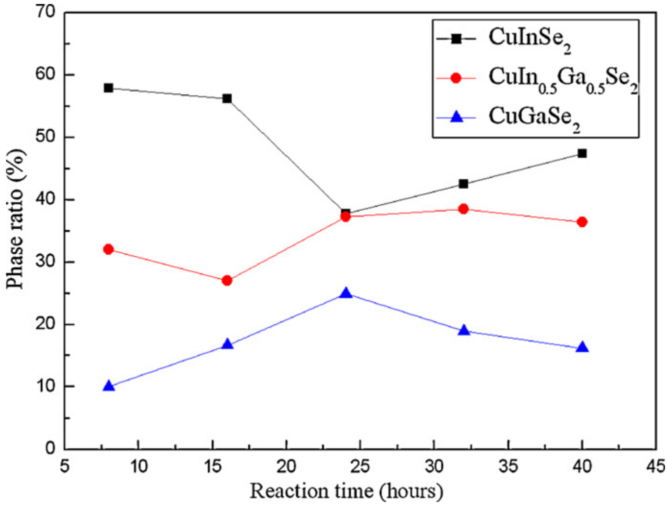

Fig. 3. Phase ratios of CIS, CIGS, and CGS with reaction time at 250 °C.

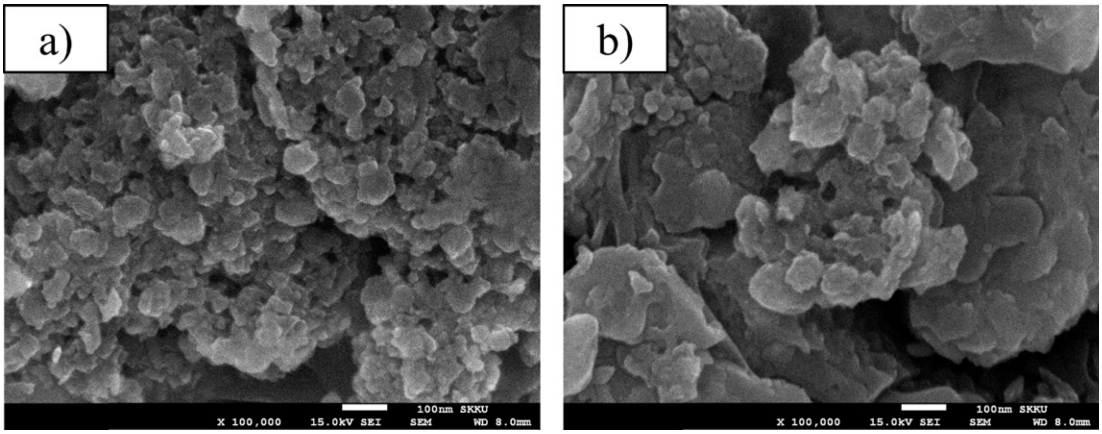

Fig. 4. Particle morphologies of synthesized powder at 250 °C with reaction time: (a) 8 h and (b) 40 h.

result also agreed with precedent study by Gu et al. [12] which reported that certain single phase with fixed ratio of In:Ga is not synthesized but CIGS phases of different ratio of In:Ga coexist in the synthesized powder, as indium can be solved completely in CGS. Though the precise ratio may not be correct, the coexistence of CIS, CGS, and CIGS could be explained sufficiently by the program. From this result, it can be known that stable single phase CIGS can hardly be synthesized with increase of reaction temperature, as the phase formation temperatures of the three phases are almost same.

Fig. 3 shows phase ratios of CIS, CGS, and CIGS calculated from the XRD patterns with variation of reaction time at 250 °C. Each phase of CIS, CGS, and CIGS was already formed at 8 h. CIS appeared to decrease till 24 h but increased again to 40 h. CIGS increased slightly up to 24 h but showed no remarkable increase or decrease afterward. CGS increased up to 24 h but decreased afterward. As a whole, the phase ratio did not change significantly and single phase CIGS was not formed. Though Chun et al. [9] did not explain these phase ratio exactly, the coexistence of three phases could be confirmed from their data. Wang et al. [13] reported the formation of single phase CIGS, but it was not synthesized and coexistence of three phases could be shown in their XRD patterns. As a result, it can be shown that single phase CIGS could hardly been synthesized by solvothermal method despite results of Chun et al. and Wang et al. The phase ratio of CIS, CGS, and CIGS did not change notably with either reaction temperature or reaction time.

Fig. 4 shows the particle shapes of synthesized powder at 250 °C with reaction time of (a) 8 h and (b) 40 h. Sizes of primary particles are about 100 °C in both (a) and (b), but those in (b) are somewhat larger than those in (a). Particles in both (a) and (b) are agglomerated seriously. During solvothermal process, among the formed solid particles, the larger ones are thought to grow with consumption of smaller ones with growth mechanism known as 'Ostwald ripening' [14].

4. Conclusions

The synthesis of CIGS powder was examined by solvothermal method. At low reaction temperature of 210 °C, CIS and CGS were formed first without CIGS. As reaction temperature increased, CIGS phases of different compositions appeared at 230 °C, but made into one stoichiometric composition at 250 °C. With increase of reaction time at 250 °C, the phase ratio did not change significantly and three phases coexisted.

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