Phase Transformation of CuIn$_x$Ga$_{1-x}$-Se$_2$ Powder by Milling and Heat Treatment†

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CuIn$_x$Ga$_{1-x}$-Se$_2$ ink and paste by milling and subsequent heat treatment to remove organic compounds contained in the thick film are to be crucial to produce dense CuIn$_x$Ga$_{1-x}$-Se$_2$ absorber layer, however, few studies has been performed to address such processes. The object of this study is to identify wet milling conditions for CuIn$_x$Ga$_{1-x}$-Se$_2$ powder and observe its phase transition and pertinent morphology change according to different heat treatments of CuIn$_x$Ga$_{1-x}$-Se$_2$. CuIn$_x$Ga$_{1-x}$-Se$_2$ powder was dispersed in planetary mill containing diethylamine as solvent and exhibited no phase transformation. CuIn$_x$Ga$_{1-x}$-Se$_2$ disappeared after annealed in air at 200 ℃ or more. In the case of Se-N$_2$-H$_2$ atmosphere, secondary phase in small portion was formed after annealed at 150 ℃ up to 300 ℃ whereas CuIn$_x$Ga$_{1-x}$-Se$_2$ was maintained above it. Dense CuIn$_x$Ga$_{1-x}$-Se$_2$ film was obtained after sintered in Se-H$_2$-N$_2$ at 800 ℃.

Key Words: CuIn$_x$Ga$_{1-x}$-Se$_2$, Solvothermal synthesis, Phase transformation, Milling process, Thick film.

INTRODUCTION

The thickness of silicon solar cell should be 100 μm or more for enough optical absorption and process application to the substrate, which accounts for its high production costs[1,2]. However, CuIn$_x$Ga$_{1-x}$-Se$_2$ (CIGS) solar cell exhibits adequate optical absorption properties with a thickness of 2-3 μm[3] and, on this account, has been increasingly developed to deliver high absorption efficiency only *via* thin film process, without a single crystal ingot as employed in silicon solar cell production[4,5]. CuIn$_x$Ga$_{1-x}$-Se$_2$ manufactured by thin film process, on the other hand, lacks film consistency due to the 4 sources including Cu, In, Ga and Se, each of which requires different deposition conditions and consequently cannot be produced in a large area wafer[5,6]. A lot of researches on thick film process to produce CuIn$_x$Ga$_{1-x}$-Se$_2$ solar cell to address such issues have been reported[7,8]. Ink or paste formed from synthesized powder with homogenous composition is printed on substrate to manufacture the thick film[9,10], which is to be sintered into dense CuIn$_x$Ga$_{1-x}$-Se$_2$ film that is serviceable as optical absorber layer. Solvothermal method is generally selected among others to synthesize CuIn$_x$Ga$_{1-x}$-Se$_2$ powder since it facilitates a homogenous size of the powder[11,12]. Liquid phase methods may induce severe aggregation among particles during the synthesis[13,14], which should requires ball mill process to eliminate the aggregation[15].

Organic compounds such as dispersant or binder is to be added in CuIn$_x$Ga$_{1-x}$-Se$_2$ powder for thick film process[16]. Binder contained in thick film, if not completely removed before sintering, is to remain as residual carbonaceous materials that may induce defects in the film and impair cell properties[17,18], which should be, in this regard, removed burn-out process during the sintering. However, nonoxides including CuIn$_x$Ga$_{1-x}$-Se$_2$ often transforms to an oxide or disappears in heat treatment in air[19] and proper burn-out conditions should be established.

This study is to observe powder phases and pertinent morphology through milling according to different solvents and to identify burn-out conditions for CuIn$_x$Ga$_{1-x}$-Se$_2$ film by changing atmosphere and temperature and consequent CuIn$_x$Ga$_{1-x}$-Se$_2$ phase transformation.

EXPERIMENTAL

Powder source and solvents for synthesis and milling are shown in Table-1. The powders of Cu, In, GaCl$_3$ and Se were used, and the solvent was used ethylenediamine. In the glove box filled with argon gas, Cu of 0.01M, In of 0.005M, Ga source of 0.005M and Se of 0.02M and were loaded into the autoclave, which was then filled with anhydrous ethylenediamine (50 cc). The reaction temperature of the autoclave was controlled from 185 ℃ for 12 h and then reacted at 230 ℃ for

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TABLE-1 CHEMICAL SOURCE AND SOLVENTS FOR SYNTHESIS AND MILLING	
Name	Speciation
Cu	99.7 %, Sigma Aldrich Co. Ltd., Japan
In	99.99 %, Sigma Aldrich Co. Ltd., Japan
GaCl$_3$	99.99 %, Sigma Aldrich Co. Ltd., Japan
Se	99.99 %, Sigma Aldrich Co. Ltd., Japan
Ethylenediamine	99.9 %, Sigmae Aldrich Co. Ltd., Japan
Acetone	99 %, Junsei Chemical Co. Ltd., Japan
Toluene	99 %, Junsei Chemical Co. Ltd., Japan
Ethanol	99 %, Daejung Chemical & Metals Co.Ltd., Korea
Xylene	99 %, Junsei Chemical Co. Ltd., Japan
Diethylamine	99 %, Junsei Chemical Co. Ltd., Japan

24 h. The synthesized CuIn$_x$Ga$_{1-x}$-Se$_2$ powders were washed with distilled ethanol to remove the by-products and then, dried at 80 ºC for 24 h.

The synthesized CuIn$_x$Ga$_{1-x}$-Se$_2$ powders were milled by planetary mill (Pulverisette 7, Fritsch GmbH, Germany). The milling solvent was using acetone, toluene, ethanol, xylene, diethylamine and ethylenediamine. The milling powder were washed with distilled ethanol to remove the by-products and then, dried at 80 ºC for 24 h. The dried powder of 5 g were dispersed in diethylamine of 30 cc with dispersant (Byk-111, BYK-chemie, Germany) by planetary mill. The CuIn$_x$Ga$_{1-x}$-Se$_2$ ink was produced from CuIn$_x$Ga$_{1-x}$-Se$_2$ solution to added diethyl-amine of 70 cc. The prepared ink was printed on the Ni coated Al$_2$O$_3$ substrates. The specimen was sintered at 800 ºC with the Se powder in atmospheric pressure in a H$_2$/N$_2$ mixed gas.

The crystal structures of synthesized powders were measured by X-ray diffractometer (PANalytical, X'pert pro, Netherlands) and the particle morphologies were observed by field emission scanning electron microscope (LSM-6700F, Jeol, Japan).

RESULTS AND DISCUSSION

Fig. 1 shows phase change in CuIn$_x$Ga$_{1-x}$-Se$_2$ phase according to milling solvent. CuIn$_x$Ga$_{1-x}$-Se$_2$ formed in secondary phase with CuSe$_2$ when acetone was applied as milling solvent. CuIn$_x$Ga$_{1-x}$-Se$_2$ and CuSe$_2$ formed in xylene or toluene. It is thought that In and Ga ion are dissolved out of CuIn$_x$Ga$_{1-x}$-Se$_2$ into ethanol during milling and then are removed during washing. It is remarkable that CuIn$_x$Ga$_{1-x}$-Se$_2$ completely disappeared in ethanol and only CuSe$_2$ remained, which was verified even after 10 min moderate milling. It has been recently reported that mechanochemical methods, among others, may synthesize CuIn$_x$Ga$_{1-x}$-Se$_2$ powders from relevant raw materials simply by ball milling[20,21], which implies that CuIn$_x$Ga$_{1-x}$-Se$_2$ phase is to be obtained only by milling. Dispersion process aforementioned may be interpreted from such aspect. CuIn$_x$Ga$_{1-x}$-Se$_2$ was observed only, without any other one in case of diethylamine employed as solvent. Diethylamine, thus, is expected to be used to mill CuIn$_x$Ga$_{1-x}$-Se$_2$ powder.

Fig. 2 exhibits phase transition of CuIn$_x$Ga$_{1-x}$-Se$_2$ powder according to time when is milled in diethylamine. After 2 h of planetary mill process, no phase transformation was observed in CuIn$_x$Ga$_{1-x}$-Se$_2$ powder. Peak intensities of CuIn$_x$Ga$_{1-x}$-Se$_2$ after the 2 h decreased compared with those of raw powder, which is considered due to powder aggregation removed
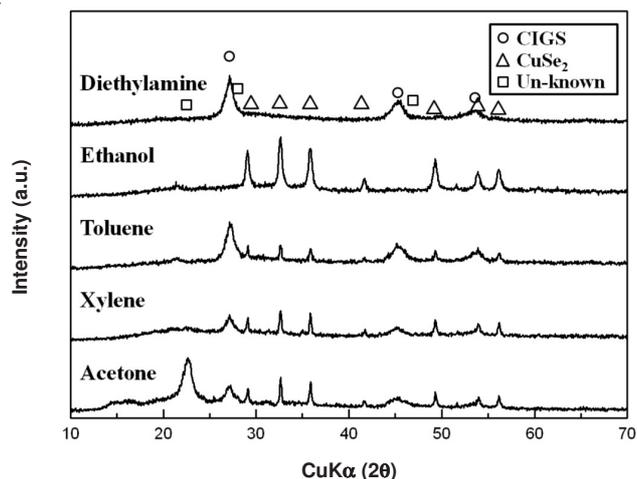
Fig. 1. Phase change in CuIn$_x$Ga$_{1-x}$-Se$_2$ (CIGS) phase according to milling solvent
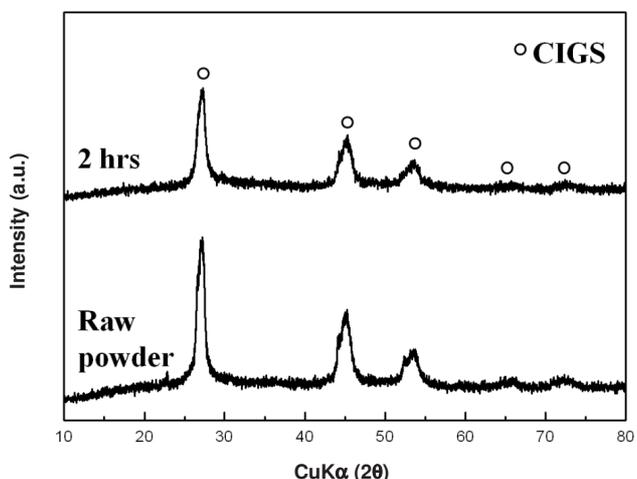
Fig. 2. Phase transition of CuIn$_x$Ga$_{1-x}$-Se$_2$ (CIGS) powder according to time when in milled in diethylamine

during the process, which decreased the size of aggregate CuIn$_x$Ga$_{1-x}$-Se$_2$ particles.

Particle shapes (a) before and (b) after milling were illustrated in Fig. 3. Primary CuIn$_x$Ga$_{1-x}$-Se$_2$ particle had a diameter approximately of 100-200 nm before milling but showed severe aggregation among particles. Secondary CuIn$_x$Ga$_{1-x}$-Se$_2$ particle was aggregated in a diameter of a few μm, which was crushed into smaller pieces after 0.5 h of milling.
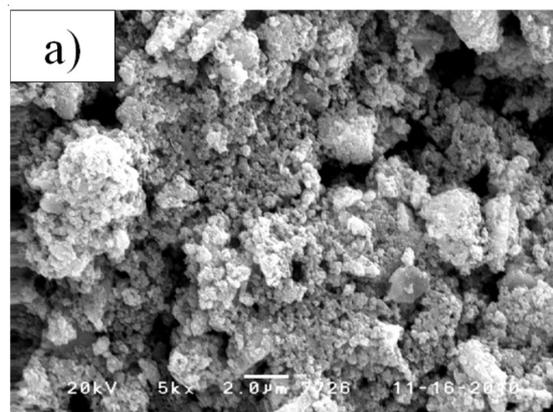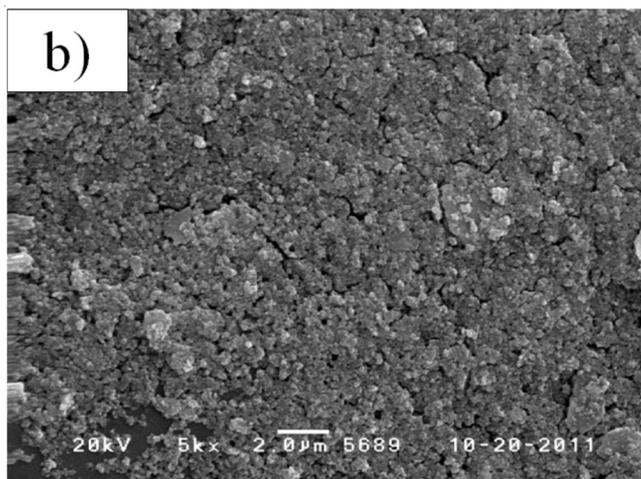
Fig. 3. Particle shapes (a) before and (b) after milling

Organic compounds such as dispersant are to be added to form ink of CuIn$_x$Ga$_{1-x}$-Se$_2$ powder. Organic compounds not burned-out adequately may induce many defects during sintering, which is to lower efficiency of the device. Burn-out process establishment is crucial in this regard. Fig. 4 shows phase transition of CuIn$_x$Ga$_{1-x}$-Se$_2$ powder according to air with annealing temperature for burn-out of organic compound. Heat treatment at 200 ℃ or more is required at large for burn-out of organic compounds. However, its phase changed to CuSe$_2$ in air over 210 ℃ while CuSe$_2$ disappeared only with amorphous phases remaining as temperature increased. This indicates that it is impossible to burn-out organic compounds in air without CuIn$_x$Ga$_{1-x}$-Se$_2$ phase transition.
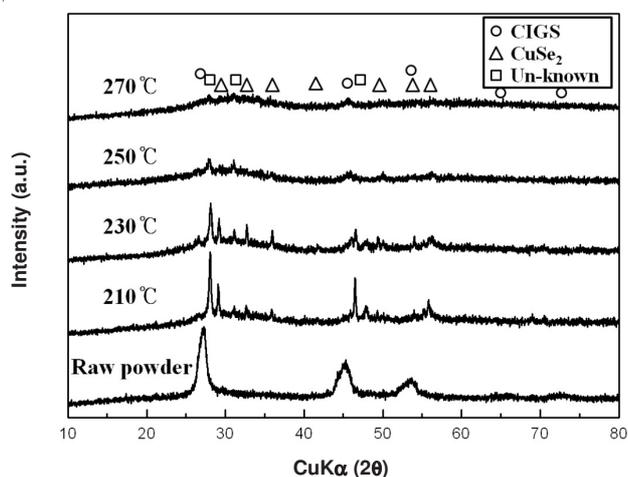
Fig. 4. Phase transition of CuIn$_x$Ga$_{1-x}$-Se$_2$ (CIGS) powder according to air with annealing temperature for burn-out of organic compounds

Fig. 5 shows phase transition of CuIn$_x$Ga$_{1-x}$-Se$_2$ powder in Se-N$_2$-H$_2$ atmosphere according to heat treatment temperature for burn-out of organic compounds. Secondary phase in small portion was observed at 150 ℃ and another unknown phase in small portion with CuSe$_2$ at 250 ℃. No other phase than CuIn$_x$Ga$_{1-x}$-Se$_2$ was observed over 350 ℃. CuIn$_x$Ga$_{1-x}$-Se$_2$ phase transformed in the range of 150-300 ℃, which indicates that the burn-out temperature should be rapidly increased from 150-300 ℃ in case of heat treatment in Se-N$_2$-H$_2$ atmosphere.
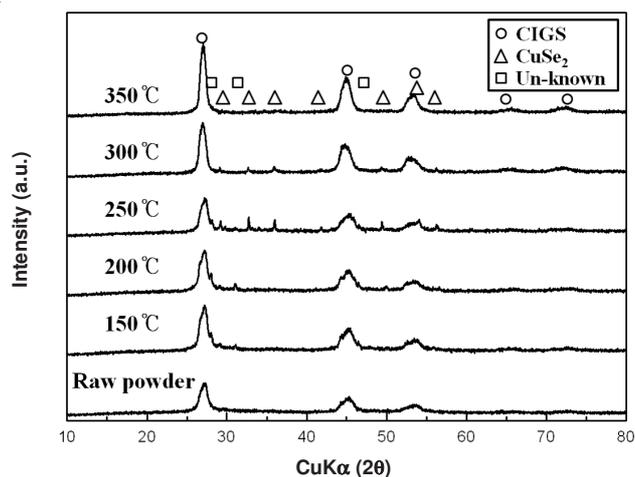
Fig. 5. Phase transition of CuIn$_x$Ga$_{1-x}$-Se$_2$ (CIGS) powder in Se-N$_2$-H$_2$ atmosphere according to heat treatment temperature for burn-out of organic compounds

Fig. 6 shows cross-sectional, (a) and plane view, (b) of CuIn$_x$Ga$_{1-x}$-Se$_2$ layer sintered in Se-N$_2$-H$_2$ atmosphere at 800 ℃. The layer was completely dense and had a thickness of *ca.* 2 µm, partially with crack on the surface, which is considered produced in drying.
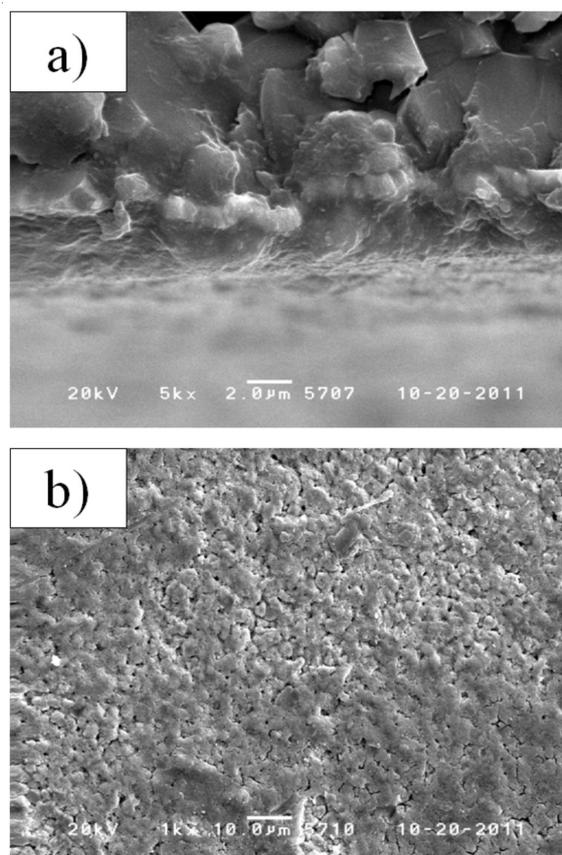
Fig. 6. (a) cross-sectional, (a) and plane view, (b) of CuIn$_x$Ga$_{1-x}$-Se$_2$ (CIGS) layer sintered in Se-N$_2$-H$_2$ atmosphere at 800 ℃

Conclusion

During CuIn$_x$Ga$_{1-x}$-Se$_2$ ink manufacturing, CuIn$_x$Ga$_{1-x}$-Se$_2$ phase disappeared after processed in planetary mill containing

a variety of solvents whereas no phase transformation was observed in milling containing diethylamine. $CuIn_xGa_{1-x}-Se_2$ was disappeared after heat-treated in air at 200 ºC or more. The secondary phase of small amount was formed after annealed in Se-N$_2$-H$_2$ at 150 up to 300 ºC whereas no phase transformation was observed above it, which indicates $CuIn_xGa_{1-x}-Se_2$ should require heat treatment in Se-H$_2$-N$_2$ at 300 ºC or more. Dense $CuIn_xGa_{1-x}-Se_2$ film was obtained after sintered in Se-H$_2$-N$_2$ at 800 ºC.

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