

# Effect of Complexing/Buffering Agents on Morphological Properties of CuInSe<sub>2</sub> Layers Prepared by Single-Bath Electrodeposition

Hana Lee<sup>1,3)</sup> · Wonjoo Lee<sup>2)</sup> · Kyungwon Seo<sup>1)</sup> · Doh-Kwon Lee<sup>3)</sup> · Honggon Kim<sup>3)\*</sup>

<sup>1)</sup>Department of Chemical Engineering, Ajou University, Suwon 442-749, Korea

<sup>2)</sup>Samsung Advanced Institute of Technology, Yong-In 446-712, Korea

<sup>3)</sup>Photo-electronic Hybrids Research Center, Korea Institute of Science and Technology (KIST), Seoul 136-791, Korea

**ABSTRACT:** For preparing a device-quality CuInSe<sub>2</sub> (CISE) light-absorbing layer by single-bath electrodeposition for a superstrate-type CISE cell, morphological properties of the CISE layers were investigated by varying concentrations of sulfamic acid and potassium biphthalate, complexing/buffering agents. CISE films were grown on an In<sub>2</sub>Se<sub>3</sub> film by applying a constant voltage of -0.5V versus Ag/AgCl for 90 min in a solution with precursors of CuCl<sub>2</sub>, InCl<sub>3</sub>, and SeO<sub>2</sub>, and a KCl electrolyte. A dense and smooth layer of CISE could be obtained with a solution containing both sulfamic acid and potassium biphthalate in a narrow concentration range of combination. A CISE layer prepared on the In<sub>2</sub>Se<sub>3</sub> film with proper concentrations of complexing/buffering agents exhibited thickness of 1.6~1.8 μm with few undesirable secondary phases. On the other hand, when the bath solution did not contain either sulfamic acid or potassium biphthalate, a CISE film appeared to contain undesirable flake-shape Cu<sub>2-x</sub>Se phases or sparse pores in the upper part of film.

**Key words:** CuInSe<sub>2</sub>, CISE, superstrate-type CuInSe<sub>2</sub> cell, electrodeposition, complexing agent, buffering agent

## 1. Introduction

Ternary and quarternary chalcopyrite compounds, such as CuInSe<sub>2</sub> (CISE), Cu(In,Ga)Se<sub>2</sub> (CIGSe), CuIn(S<sub>x</sub>,S<sub>2-x</sub>)<sub>2</sub> (CISES), and CuGaSe<sub>2</sub> (CGSe), have attracted considerable attention as excellent materials in inorganic thin film solar cells due to their high absorption coefficients (~10<sup>5</sup> cm<sup>-1</sup>) and low cost<sup>1,2)</sup>. A high conversion efficiency near 20% was achieved with a CIGSe solar cell of a laboratory scale prepared by a vacuum process<sup>3,4)</sup>. CISE or CIGSe films can be prepared by various methods including coevaporation<sup>5)</sup>, sputtering<sup>6)</sup>, electrodeposition<sup>7)</sup>, spraying<sup>8)</sup>, printing<sup>8)</sup>, molecular beam epitaxy<sup>9)</sup>, and so on. Among these, the electrodeposition has been considered a promising approach from the view points of a non-vacuum and low-cost process, formation of a dense and smooth film, and large area production. CIGSe solar cells prepared by electrodeposition have already reached efficiencies over 11.5% on a laboratory scale and of around 7% on a module scale<sup>10)</sup>. By

adding the physical vapor deposition (PVD) of In and Ga onto the electrodeposited CIGSe film to adjust the atomic ratios of Cu, In, Ga, and Se, an enhanced cell efficiency over 15% was achieved<sup>11, 12)</sup>. However, these cells have a configuration consisting of glass/Mo/CIGSe/CdS/ZnO, which still needs some cost-intensive vacuum steps, such as sputtering of Mo, i-ZnO and Al-doped ZnO. A superstrate structure, which is the reverse of conventional figures, has been proposed for a cheaper process for CIGSe cells. Superstrate-type cells prepared by the evaporation technique showed efficiencies over 8%<sup>13, 14)</sup>, and ones prepared by electrodeposition of CISE films on In<sub>2</sub>Se<sub>3</sub> yielded efficiencies of 2.9~3.6%<sup>15-18)</sup>.

In order to produce high-efficiency CISE or CIGSe solar cells by electrodeposition, there are a number of difficulties to be overcome, including the structural and morphological properties of films, the control of compositional depth profile, and the avoidance of co-deposition of oxides. In particular, the growth of undesirable secondary phases, representatively copper selenides (Cu<sub>2-x</sub>Se), usually leads to the formation of Cu-rich films<sup>19)</sup>. The excessive Cu<sub>2-x</sub>Se phases are highly conductive and apt to produce shunt paths, which negatively influence the

\*Corresponding author: hkim@kist.re.kr

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device efficiencies. To obtain device-quality film,  $\text{Cu}_{2-x}\text{Se}$  on the surface of CIGSe or CISE films is sometimes removed by chemical etching with KCN<sup>20-23</sup>). However, it is ideal and an ultimate goal to minimize  $\text{Cu}_{2-x}\text{Se}$  phases during the electro-deposition of CIGSe or CISE films. Therefore, a facile and effective method is necessary to inhibit the growth of  $\text{Cu}_{2-x}\text{Se}$  phases.

An effective method to suppress the overgrowth of  $\text{Cu}_{2-x}\text{Se}$  phases during electrodeposition is the utilization of complexing agents in the baths solution. Various complexing agents have been proposed for the electrodeposition of CISE or CIGSe, such as citrate<sup>24,25</sup>), triethanolaminex<sup>26,27</sup>), ethylenediaminetetraacetic acid<sup>28</sup>), ethylenediamine<sup>29</sup>), thiocyanate<sup>30, 31</sup>), benzotriazole<sup>32</sup>). These complexing agents are widely utilized in copper plating baths and can form stable complexes with copper in basic solutions. But complexing abilities of these agents on metal ions are dramatically reduced by  $\text{H}^+$  concentration. There are not many suitable agents for acidic solutions of pH 1.5~3 due to the easy reduction of  $\text{HSeO}_3^-$  in the CISE or CIGSe baths. Thus, it is still interesting to search a proper acidic complexing agent for inhibiting the overgrowth of  $\text{Cu}_{2-x}\text{Se}$  phases. Recently, sulfamic acid was suggested as a complexing agent for one-step electro-deposition of CIGSe in acidic solution.<sup>33</sup>) Sodium sulfamate and metal ions form metal complexes of  $\text{Metal}(\text{NH}_2\text{SO}_3)_3^{2-}$  in the precursor solution. The degree of metal complex formation influences the diffusion and electro-chemical activity of the metal ions during electrodeposition. Therefore, the chemical and physical properties of metal complexes can determine the atomic composition, structure, density and morphology of CIGSe or CISE films.

On the other hand, structural and morphological properties of the CIGSe or CISE films were also strongly influenced by pH of the electrodeposition baths solution<sup>34</sup>). A pH buffer solution can attenuate precipitation or deposition of hydroxides during film growth. In addition, the control of pH allows preserving electrolytic baths for several weeks. The use of pH buffered sulfate-based baths solution has resulted in 3.6% efficiency of the CISE devices without a subsequent vacuum processing to adjust composition. Although the efficiency is still low in comparison with vacuum process-based CISE cells, the efficiency can be improved by film structure and morphology. In this paper, we are investigating the morphological properties of electrodeposited CISE absorber layers on an  $\text{In}_2\text{Se}_3$  film using different baths

solutions containing various concentrations of sulfamic acid and potassium biphthalate.

## 2. Experiments

### 2.1 Materials

Chemicals for the metallic precursors,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{InCl}_3$ ,  $\text{SeO}_2$ , and the supporting electrolytes, KCl and LiCl, were supplied from Aldrich Co. and used without further purification. Indium tin oxide (ITO,  $10\Omega/\text{square}$ ) glasses were obtained from Samsung Corning Co., Korea.

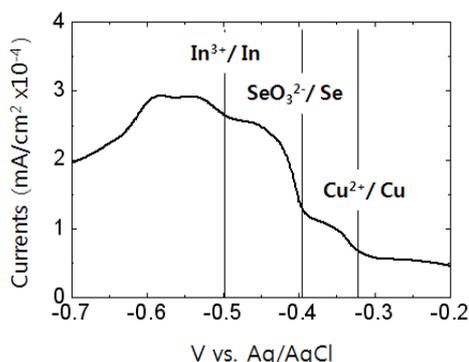
### 2.2 Electrodeposition of film

Before electrodeposition of metallic components for  $\text{In}_2\text{Se}_3$  and  $\text{CuInSe}_2$  (CISE) films, the working electrode, ITO glass ( $1.0 \times 1.5 \text{ cm}^2$ ), was cleaned in an ultrasonic baths successively with a neutral detergent, isopropylalcohol, acetone and again isopropylalcohol. Firstly,  $\text{In}_2\text{Se}_3$  was electrodeposited on the cleaned ITO glass, and CISE was electrodeposited on the  $\text{In}_2\text{Se}_3$  film formed. The electrodeposition of  $\text{In}_2\text{Se}_3$  and CISE was carried out using a potentiostat/galvanostat (CHI 620A Electrochemical Analyzer, CH Instruments, Austin, TX, USA) at room temperature without stirring. An Ag/AgCl electrode and Pt plate were used as a reference electrode and a counter electrode, respectively. For  $\text{In}_2\text{Se}_3$  electrodeposition, a baths solution was prepared with 2.4 mM of  $\text{InCl}_3$ , 4.8mM of  $\text{SeO}_2$  and 0.24M LiCl as an electrolyte in deionized distilled  $\text{H}_2\text{O}$  without any complexing agent. A thin  $\text{In}_2\text{Se}_3$  film of ~50 nm thickness was electrodeposited on the ITO electrode surface by applying a constant voltage of -0.6V vs. Ag/AgCl for 40 min. For CISE electrodeposition, the baths solution composed of 2.56mM of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , 2.4mM of  $\text{InCl}_3$ , 4.8mM of  $\text{SeO}_2$  and 0.24M KCl as an electrolyte in deionized distilled  $\text{H}_2\text{O}$  with sulfamic acid and potassium biphthalate was prepared in a single bath. CISE films were grown on the  $\text{In}_2\text{Se}_3$  film by applying constant -0.5V vs. Ag/AgCl. The structure and surface morphology of  $\text{In}_2\text{Se}_3$  and CISE films were characterized using a field emission scanning electron microscopy (FE-SEM, Hitachi S-4100). The formation of CISE and  $\text{Cu}_{2-x}\text{Se}$  phases and the atomic composition of the film were evaluated using a x-ray diffraction (XRD, Rigaku D/MAX 2500) and energy dispersive spectroscopy (EDS, EMAX-Horiba), respectively.

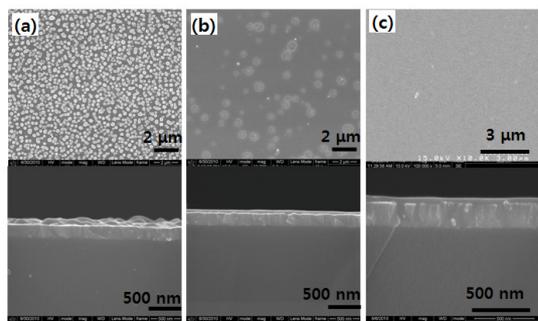
### 3. Results and Discussion

#### 3.1 Deposition Potentials

A cyclic voltammogram of CISE baths solution was conducted to determine proper reduction potentials of ions to elements for electrodeposition. As shown in Fig. 1, the reduction potentials of  $\text{Cu}^{2+}$  to Cu,  $\text{SeO}_3^{2-}$  to Se, and  $\text{In}^{3+}$  to In were measured as -0.34V, -0.4V, and -0.5V vs. Ag/AgCl, respectively. The reduction potentials measured were a little bit different from the values reported.<sup>33)</sup> The deviation of reduction potentials from the theoretically expected values could be caused by various factors such as the concentration of electrolyte, pH of the solution, relative size of the substrate to the counter Pt electrode, the type of supporting electrolyte, etc. Even though the reduction potentials were assigned, the actual electrodeposition of each element started to occur from the potential slightly below its measured value. For simultaneous electrodeposition of three components in a single baths, a potential around -0.5V vs. Ag/AgCl was found suitable.



**Fig. 1.** A linear sweep voltammogram of CISE baths solution at a scan rate of 50 mV/s.



**Fig. 2.** SEM images of  $\text{In}_2\text{Se}_3$  thin films on the ITO glass by applying constant voltages of (a) -0.5V vs. Ag/AgCl for 10 min, (b) -0.6V for 10 min, and (c) -0.6V for 40 min; (Upper) surface, (Lower) cross-section.

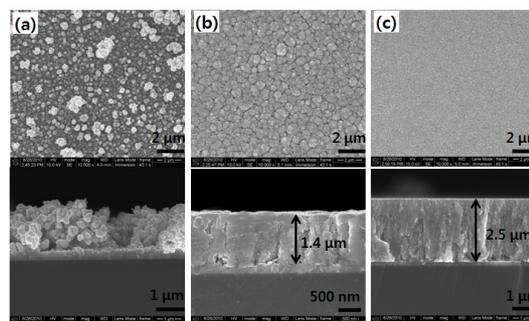
#### 3.2 Preparation of $\text{In}_2\text{Se}_3$ film

Before depositing the CISE absorption layer, an  $\text{In}_2\text{Se}_3$  film was deposited on the ITO glass as a buffer layer for a superstrate-type solar cell, which would replace a toxic CdS buffer layer<sup>15, 35)</sup>. Fig. 2 shows SEM images of  $\text{In}_2\text{Se}_3$  films electrodeposited on the ITO surface at -0.5V and -0.6V vs. Ag/AgCl. While an  $\text{In}_2\text{Se}_3$  film stacked with island-shape particles of 250~500 nm in size was formed at -0.5V (Fig. 2 (a)), a thin continuous  $\text{In}_2\text{Se}_3$  film was formed by applying -0.6V (Fig. 2 (b)). As the deposition time increased at constant -0.6V, more compact and smooth  $\text{In}_2\text{Se}_3$  film covered the ITO surface. As shown in Fig. 2 (c), the thickness of  $\text{In}_2\text{Se}_3$  layer deposited for 40 min was about 60 nm.

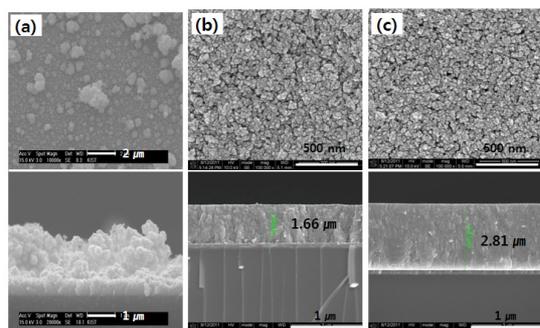
#### 3.3 Electrodeposition of CISE film on $\text{In}_2\text{Se}_3/\text{ITO}$

Firstly, CISE films were formed on the  $\text{In}_2\text{Se}_3$  film by electrodeposition in a single baths solution having the precursors of 2.56mM of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , 2.4mM of  $\text{InCl}_3$ , 4.8mM of  $\text{SeO}_2$ , the electrolyte of 0.24M KCl, and the complexing/buffering agents of 0.01M sulfamic acid and 0.01M potassium bipthalate at different potentials. Differently from the electrodeposition of  $\text{In}_2\text{Se}_3$  on ITO films, a continuous and smooth CISE film on the  $\text{In}_2\text{Se}_3$  film was formed by applying -0.5V vs. Ag/AgCl (Fig. 3 (b)), while randomly grown particles were stacked at -0.6V (Fig. 3 (a)). As the electrodeposition time increased, a smoother, denser and thicker CISE film was obtained at the potential of -0.5V (Fig. 3 (c)). Therefore, a constant potential of -0.5V seemed proper for the single-bath CISE electrodeposition.

Secondly, CISE films were formed on  $\text{In}_2\text{Se}_3/\text{ITO}$  with various concentrations of Cu, In, and Se precursors in order to find out the proper range of precursor concentrations. The ratio



**Fig. 3.** SEM images of CISE films on the  $\text{In}_2\text{Se}_3$  thin films by applying constant voltages of (a) -0.6V vs. Ag/AgCl for 60 min, (b) -0.5V for 60 min and (c) -0.5V for 120 min; (Upper) surface, (Lower) cross-section.



**Fig. 4.** SEM images of ClSe films on  $\text{In}_2\text{Se}_3/\text{ITO}$  electrodeposited at  $-0.5\text{V}$  vs.  $\text{Ag}/\text{AgCl}$  for 90 min with various precursor concentrations and with sulfamic acid and potassium biphthalate of 10 mM: The concentrations of  $\text{CuCl}_2/\text{InCl}_3/\text{SeO}_2$  are (a) 1.28/1.2/2.4 mM, (b) 2.56/2.4/4.8 mM, and (c) 3.84/3.6/7.2 mM; (Upper) surface, (Lower) cross-section.

of Cu, In and Se precursors in the baths was fixed at 1.07/1/2, and the concentrations of both sulfamic acid and potassium biphthalate were maintained at 10 mM of each. As shown in Fig. 4, a continuous ClSe film could not be obtained from the baths of low-concentration precursors (Fig. 4 (a)), while a dense and uniform ClSe films were successfully obtained from the baths having high precursor concentrations (Fig. 4 (b) and (c)).

The result indicated that there are concentration boundaries of precursors for forming a uniform ClSe film, and it proposed 2.56/2.4/4.8 mM of  $\text{CuCl}_2/\text{InCl}_3/\text{SeO}_2$  as the proper concentrations of low limit. In addition, with a baths solution having higher precursor concentrations, a continuous and dense ClSe film could be produced faster, and its thickness increased nearly in proportion to the precursor concentrations. However, from the point of elemental composition in ClSe films, the content of Cu increased and that of Se decreased with the baths having higher precursor concentrations. Namely, a baths with high precursor concentrations could induce a Cu-rich ClSe film as shown in Table 1, even though the ClSe film could be formed in a fast way.

### 3.4 Effect of Complexing/Buffering Agents on ClSe Film Formation

Based on the proper electrodeposition conditions obtained above, ClSe films were electrodeposited on  $\text{In}_2\text{Se}_3/\text{ITO}$  at  $-0.5\text{V}$  vs.  $\text{Ag}/\text{AgCl}$  for 90 min using different baths solutions having various concentrations of complexing/buffering agents as listed in Table 2. For the concentrations of sulfamic acid and potassium biphthalate used, pH of the baths solution was found

**Table 1.** Effect of precursor concentration on the elemental composition in ClSe films

Precursor Concentration (mM)	Compositional Ratio*	
	Cu/In	Se/(Cu+In)
$\text{CuCl}_2 / \text{InCl}_3 / \text{SeO}_2$		
2.56 / 2.4 / 4.8	1.05	1.11
3.84 / 3.6 / 7.2	1.09	1.04

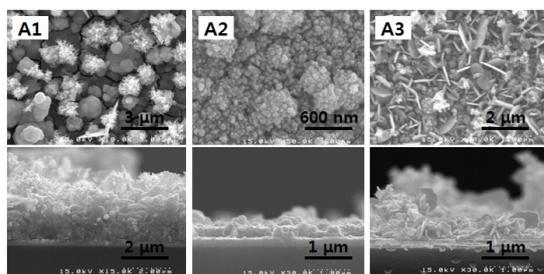
\* The compositional ratios were obtained from EDS analysis data.

**Table 2.** Concentrations of complexing/buffering agents and pH of the baths solutions

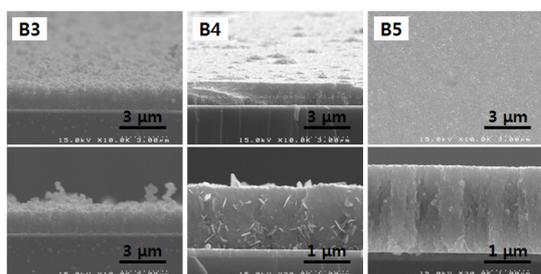
Bath solution	Sulfamic acid	Potassium biphthalate	pH
A1	-	-	2.7
A2	10 mM	-	1.8
A3	-	10 mM	3.1
B1	1 mM	1 mM	2.5
B2	3 mM	3 mM	2.5
B3	5 mM	5 mM	2.4
B4	7 mM	7 mM	2.4
B5	10 mM	10 mM	2.0~2.1
C1	10 mM	1 mM	1.9
C2	10 mM	3 mM	2.0
C3	10 mM	5 mM	2.0
C4	10 mM	7 mM	2.0~2.1
D1	1 mM	10 mM	2.8
D2	3 mM	10 mM	2.6
D3	5 mM	10 mM	2.4
D4	7 mM	10 mM	2.1
E1	50 mM	-	1.3
E2	50 mM	10 mM	1.3
E3	50 mM	50 mM	2.0
E4	30 mM	30 mM	2.0
E5	10 mM	50 mM	2.8
E6	-	50 mM	3.3

in the acidic range of 1.3~3.3. It tended to be more acidic as more sulfamic acid was involved, and less acidic as more potassium biphthalate was mixed. High concentrations of sulfamic acid and potassium biphthalate, such as 50 mM each, remarkably induced the precipitation of metallic precursors. The SEM images of electrodeposited ClSe layers on  $\text{In}_2\text{Se}_3/\text{ITO}$  are shown in Fig. 5 through Fig. 9.

Without any complexing/buffering agent, a rough ClSe film was formed with randomly grown particles of 100~1000 nm in size and its thickness was 3.1~3.7  $\mu\text{m}$ . (Fig. 5 A1) When the baths solution contained sulfamic acid solely (A2), pH of the solution was ~1.8. The surface of ClSe film seemed to be



**Fig. 5.** SEM images of CISE films on  $\text{In}_2\text{Se}_3/\text{ITO}$  electro-deposited at  $-0.5\text{V}$  vs.  $\text{Ag}/\text{AgCl}$  for 90 min; [A1] without sulfamic acid and potassium biphthalate, [A2] solely with 10 mM sulfamic acid, [A3] solely with 10 mM potassium biphthalate; (Upper) surface, (Lower) cross-section.

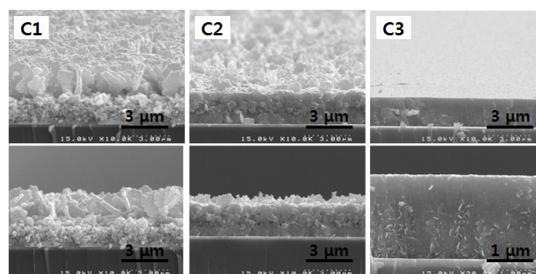


**Fig. 6.** SEM images of CISE films with same concentrations of sulfamic acid and potassium biphthalate; [B3] 5 mM each, [B4] 7 mM each, [B5] 10 mM each; (Upper) surface, (Lower) cross-section.

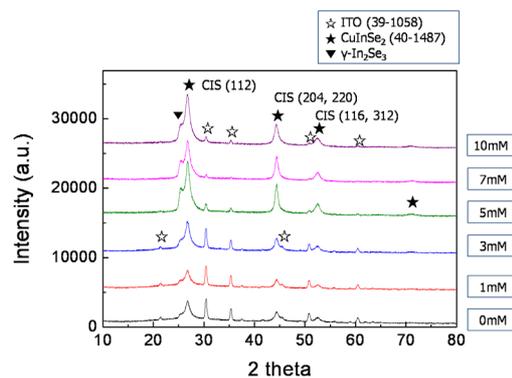
connected by particles of 200~300 nm in size, which had smaller particles of 30~60 nm growing on them. Even though the surface did not seem to have cleavages or holes, its cross-sectional images showed that a dense and continuous CISE film was not formed. When the bath solution contained potassium biphthalate solely without sulfamic acid (A3), pH of the solution was ~3.1. The surface morphology exhibited a very poor CISE film with lots of flakes of 50~60 nm in thickness and 300~600 nm in diagonal length. The flakes seemed to be  $\text{Cu}_{2-x}\text{Se}$  phases<sup>13</sup>.

When the bath solution contained both sulfamic acid and potassium biphthalate in the same amount, the CISE film got dense and had smooth surface from concentrations of 5 mM each. (Fig. 6) When 10 mM of each sulfamic acid and potassium biphthalate was used, a desirable CISE film with dense structure of 1.6~1.8  $\mu\text{m}$  thickness was obtained. (Fig. 6 B5) The surface images showed a well-developed CISE film, which was continuously connected by tightly packed particles. Its cross-sectional SEM images showed very few flakes of  $\text{Cu}_{2-x}\text{Se}$  phases both inside and on top of the CISE film.

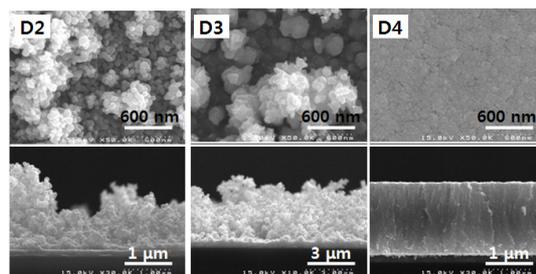
When the concentration of sulfamic acid was fixed at 10 mM, a denser and more continuous CISE film was formed with



**Fig. 7.** SEM images of CISE films prepared with 10 mM sulfamic acid and various concentrations of potassium biphthalate; [C1] 1 mM, [C2] 3 mM, [C3] 5 mM; (Upper) surface, (Lower) cross-section.

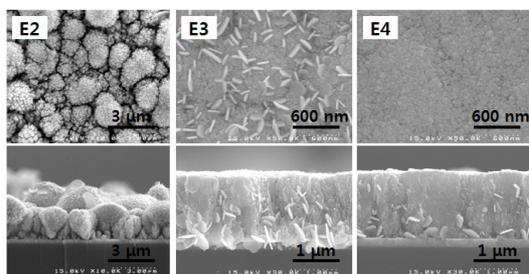


**Fig. 8.** XRD analysis of CISE films on  $\text{In}_2\text{Se}_3/\text{ITO}$  electro-deposited with 10 mM sulfamic acid and various concentrations of potassium biphthalate;  $-0.5\text{V}$  vs.  $\text{Ag}/\text{AgCl}$  for 90 min.

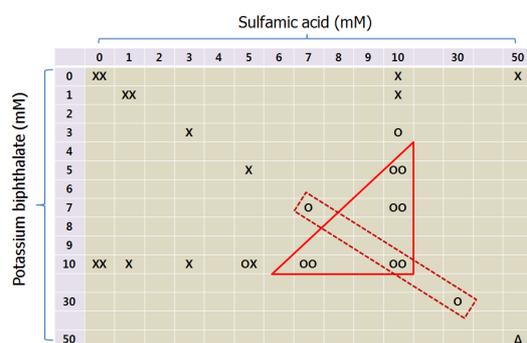


**Fig. 9.** SEM images of CISE films prepared with 10 mM potassium biphthalate and various concentrations of sulfamic acid; [D2] 3 mM, [D3] 5 mM, [D4] 7 mM; (Upper) surface, (Lower) cross-section.

potassium biphthalate of more than 5 mM. (Fig. 7 C3) This was also confirmed by the gradual decrease of ITO and  $\text{In}_2\text{Se}_3$  peaks in XRD analysis of CISE films as the increase of potassium biphthalate concentration up to 10 mM. (Fig. 8) When the concentration of potassium biphthalate was fixed at 10 mM, a dense and continuous CISE film was getting formed with sulfamic acid more than 7 mM. (Fig. 9 D4) This result indicated that the formation of CISE film was more sensitive to the concentration of sulfamic acid rather than that of potassium



**Fig. 10.** SEM images of ClSe films prepared with high concentration of sulfamic acid and potassium biphthalate; [E2] 50/10 mM, [E3] 50/50 mM, [E4] 30/30 mM; (Upper) surface, (Lower) cross-section.



**Fig. 11.** A proper concentration range of sulfamic acid and potassium biphthalate for electrodeposition of ClSe films with a solution containing 2.56mM  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , 2.4mM  $\text{InCl}_3$ , 4.8mM  $\text{SeO}_2$ , and 0.24M KCl at -0.5V vs. Ag/AgCl; oo suggested to form a continuous film, o usable,  $\Delta$  usable but precipitated, ox not recommended, x rough film with random particles, xx no film formation.

biphthalate.

Even when the concentrations of sulfamic acid and potassium biphthalate were increased up to 50 mM by keeping the same ratio, thereby keeping the pH around 2, dense and continuous ClSe films could be obtained. (Fig. 10 E3, E4) However, as the concentrations of sulfamic acid and potassium biphthalate increased more than 30 mM each, the precipitates tended to form in the solution. (Table 2 E1, E3, E5, E6) When the concentration of sulfamic acid was as high as 50 mM but that of potassium biphthalate was far low, metallic particles grew in a bundle of cauliflower-like shape. (Fig. 10 E2)

With a sufficient amount of both sulfamic acid and potassium biphthalate more than 7 mM each, a dense and continuous ClSe film could be obtained (concentrations of sulfamic acid and potassium biphthalate: B4 (7/7 mM), B5 (10/10 mM), C3 (10/5), C4 (10/7 mM), D4 (7/10 mM)). Uniform ClSe films with few secondary phases could be obtained in an acidic condition

of pH 2.0~2.2. Even though pH of the baths solution could be controlled in the proper acidic range of 2.0~2.2 by keeping the concentration ratio of sulfamic acid and potassium biphthalate around 1:1, more flakes of  $\text{Cu}_{2-x}\text{Se}$  secondary phases were produced with higher concentration than 10 mM of either sulfamic acid or potassium biphthalate. The formation of more  $\text{Cu}_{2-x}\text{Se}$  secondary phases induced the reduction of In content in the ClSe film remarkably below the stoichiometric composition. The amount of flakes also increased when the concentration of sulfamic acid was so low. When the electrodeposition was conducted with very low concentration of either sulfamic acid or potassium biphthalate (Table 2 B1, B2, C1, D1, and D2), a continuous film-shape ClSe did not form. Instead, a layer of uneven thickness, in which metallic particles or plates were randomly stacked, covered the  $\text{In}_2\text{Se}_3$  surface. A proper concentration range of sulfamic acid and potassium biphthalate could be proposed as in Fig. 11. From this result, we could suggest that the most suitable concentrations of sulfamic acid and potassium biphthalate for forming a dense and continuous ClSe film as well as for avoiding fast precipitation of metal precursors in the baths would be nearly the same moles as the summed moles of Cu, In, and Se precursors.

#### 4. Conclusions

Morphological properties of ClSe absorption layers on the  $\text{In}_2\text{Se}_3$  film were investigated by different baths solutions containing sulfamic acid and potassium biphthalate as complexing and buffering agents. Before the growth of ClSe film, a thin, compact and smooth  $\text{In}_2\text{Se}_3$  film was obtained by applying a constant voltage of -0.6V vs. Ag/AgCl for 40 min. Its thickness was ca. 60 nm. A desirable ClSe film was obtained by applying a constant voltage of -0.5V vs. Ag/AgCl with simultaneously using sulfamic acid and potassium biphthalate. The baths solution was suggested to contain nearly the same concentrations of sulfamic acid and potassium biphthalate in a range around 10 mM, which was nearly the same moles of the sum of Cu, In, and Se precursors. The ClSe films prepared in the solution of pH 2.0~2.2 did not possess many flake structures of  $\text{Cu}_{2-x}\text{Se}$  secondary phases inside the ClSe film and noticeable cleavages or pores on the surface. The thickness of this dense film was 1.6~1.8  $\mu\text{m}$ . It was revealed that the simultaneous use of sulfamic acid and potassium biphthalate in a proper ratio and

concentrations would induce a continuous, dense and uniform CISE film with few or no  $\text{Cu}_{2-x}\text{Se}$  phases. It is expected that the CISE films on  $\text{In}_2\text{Se}_3$  with few  $\text{Cu}_{2-x}\text{Se}$  phases will contribute in fabricating a device-quality CISE absorber for high efficiency solar cells by avoiding the possible defects induced during the post KCN etching of the secondary phases.

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## References

1. U. P. Singh and S. P. Patra, "Progress in polycrystalline thin-film  $\text{Cu}(\text{In,Ga})\text{Se}_2$  solar cells," *Int. J. Photoenergy*, Vol. 2010, pp 1-19, 2010.
2. A. M. Hermann, R. Westfall, and R. Wind, "Low-cost deposition of  $\text{CuInSe}_2$  (CIS) films for  $\text{CdS/CIS}$  solar cells," *Sol. Energy Mater. Sol. Cells*, Vol. 52, pp 355-360, 1998.
3. I. Repins, M. A. Contreras, B. Egaas, C. DeHart, J. Scharf, C. L. Perkins, B. To, and R. Noufi, "19.9%-efficient  $\text{ZnO/CdS/CuInGaSe}_2$  solar cell with 81.2% fill factor," *Prog. Photovolt: Res. Appl.*, Vol. 16, pp. 235-239, 2008.
4. P. Jackson, D. Hariskos, E. Lotter, S. Paetel, R. Wuerz, R. Menner, W. Wischmann, and M. Powalla, "New world record efficiency for  $\text{Cu}(\text{In,Ga})\text{Se}_2$  thin-film solar cells beyond 20%," *Prog. Photovolt: Res. Appl.*, Vol. 19, pp. 894-897, 2011.
5. G. Voorwinden, R. Kniese, and M. Powalla, "In-line  $\text{Cu}(\text{In,Ga})\text{Se}_2$  co-evaporation processes with graded band gaps on large substrates," *Thin Solid Films* Vol. 431-432, pp. 538-542, 2003.
6. R. Wuerz, A. Eicke, M. Frankenfeld, F. Kessler, M. Powalla, P. Rogin, and O. Yazdani-Assl, "CIGS thin-film solar cells on steel substrates," *Thin Solid Films*, Vol. 517, pp. 2415-2418, 2009.
7. W. Lee, J. Lee, W. Yi, and S.-H. Han, "Electric-field enhancement of photovoltaic devices: A third reason for the increase in the efficiency of photovoltaic devices by carbon nanotubes," *Adv. Mater.* Vol. 22, No. 20, pp. 2264-2267, 2010.
8. M. Kemell, M. Ritala, and M. Leskela, "Thin film deposition methods for  $\text{CuInSe}_2$  solar cells," *Crit. Rev. Solid. State Mater. Sci.*, Vol. 30, pp. 1-31, 2005.
9. Th. Hahn, H. Metzner, J. Cieslak, J. Eberhardt, U. Reislohner, J. Kraußlich, F. Wunderlich, S. Siebentritt, and W. Witthuhn, "Epitaxial  $\text{Cu}(\text{In,Ga})\text{S}_2$  thin film solar cells," *J. Phys. Chem. Solids*, Vol. 66, pp. 1899-1902, 2005.
10. S. Tauniera, J. Sixx-Kurdia, P. P. Granda, A. Chomonta, O. Ramdania, L. Parissia, P. Panheleuxa, N. Naghavia, C. Huberta, M. Ben-Faraha, J. P. Fauvarquea, J. Connollya, O. Roussela, P. Mogensenb, E. Mahe' b, J. F. Guillemolesa, D. Lincota, and O. Kerrec, " $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$  solar cells and modules by electrodeposition," Vol. 480-481, pp. 526-531, 2005.
11. R. N. Bhattacharya, W. Batchelor, J. F. Hiltner, and J. R. Sites, "Thin-film  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  photovoltaic cells from solution-based precursor layers," *Applied Physics Letters*, Vol. 75, No. 10, pp. 1431-1433, 1999.
12. R. N. Bhattacharyaa, J. F. Hiltnerb, W. Batchelora, M. A. Contrerasa, R. N. Noufi, and J. R. Sites, "15.4%  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ -based photovoltaic cells from solution-based precursor films," *Thin Solid Films* Vol. 361-362, pp. 396-399, 2000.
13. T. Nakada, N. Okano, Y. Tanaka, H. Fukuda and A. Kunioka, "Superstrate-type  $\text{CuInSe}_2$  solar cells with chemically deposited  $\text{CdS}$  window layers," 1st WCPEC (24th IEEE Photovoltaic Specialists Conference, Hawaii, IEEE, Picataway, p95, 1994.
14. T. Nakada, T. Kume, and A. Kunioka, "Superstrate-type  $\text{CuInSe}_2$ -based thin film solar cells by a low-temperature process using sodium compounds," *Sol. Energy Mater. Sol. Cells.*, Vol. 50, pp. 97-103, 1998.
15. A. Kampmann, A. Abken, G. Leimkuhler, J. Rechid, V. Stittinger, T. Wietler, and R. Reineke-Koch, "A cadmium-free  $\text{CuInSe}_2$  superstrate solar cell fabricated by electrodeposition using a  $\text{ITO/In}_2\text{Se}_3/\text{CuInSe}_2/\text{Au}$  structure," *Prog. Photovolt: Res. Appl.*, Vol. 7, pp. 129-135, 1999.
16. A. Kampmann, V. Stittinger, J. Rechid, and R. Reineke-Koch, "Large area electrodeposition of  $\text{Cu}(\text{In,Ga})\text{Se}_2$ ," *Thin Solid Films*, Vol. 361-362, pp. 309-313, 2000.
17. S. Ikeda, R. Kamai, T. Yagi, and M. Matsumura, "Electrochemical synthesis of  $\text{CuIn}(\text{Se,S})_2$  layer for thin-film solar cell with a superstrate configuration," *J. Electrochem. Soc.*, Vol. 157(1), pp. 1B99-B103, 2010.
18. S. Ikeda, R. Kamai, S.M. Lee, T. Yagi, T. Harada, and M. Matsumura, "A superstrate solar cell based on  $\text{In}_2(\text{Se,S})_3$  and  $\text{CuIn}(\text{Se,S})_2$  thin films fabricated by electrodeposition combined with annealing," *Sol. Energy Mater. Sol Cells*, Vol. 95, pp. 1446-1451, 2011.
19. W. Witte, R. Kniese, and M. Powalla, "Raman investigations of  $\text{Cu}(\text{In,Ga})\text{Se}_2$  thin films with various copper contents," *Thin Solid Films*, Vol. 517, pp. 867-869, 2008.
20. S. Niki, P. J. Fons, A. Yamada, Y. Lacroix, H. Shibata, and H. Oyanagi, "Effects of the surface  $\text{Cu}_{2-x}\text{Se}$  phase on the growth and properties of  $\text{CuInSe}_2$  films," *Applied Physics Letters*, Vol. 74, No. 11, pp. 1630-1632, 1999.
21. M. E. Calixto, K. D. Dobson, B. E. McCandless, and R. W. Birkmire, "Controlling growth chemistry and morphology of single-bath electrodeposited  $\text{Cu}(\text{In,Ga})\text{Se}_2$  thin films for photovoltaic application," *J. Electrochem. Soc.*, Vol. 153, No. 6, pp. G521-G528, 2006.
22. T. Delsol, M. C. Simmonds, and I. M. Dharmadasa, "Chemical etching of  $\text{Cu}(\text{In,Ga})\text{Se}_2$  layers for fabrication of electronic de-

- vices," *Sol. Energy Mater. Sol. Cells*, Vol. 77, pp. 331-339, 2003.
23. Y. I. Park, D. Kim, K. Seo, J. H. Jeong, and H. Kim, "Composition control of a light absorbing layer of CuInSe<sub>2</sub> thin film solar cells prepared by electrodeposition," *J. KIEEME*, Vol. 26, No. 3, pp. 232-239, 2013.
  24. K. Bouabid, A. Ihlala, A. Manar, A. Outzourhit, and E. L. Ameziane, "Effect of deposition and annealing parameters on the properties of electrodeposited CuIn<sub>1-x</sub>GaxSe<sub>2</sub> thin films," *Thin Solid Films*, Vol. 488, pp. 62-67, 2005.
  25. F. Chraïbi, M. Fahoume, A. Ennaoui, and J. L. Delplancke, "Influence of citrate ions as complexing agent for electrodeposition of CuInSe<sub>2</sub> thin films," *Phys. Stat. Sol. (a)*, Vol. 186, No. 3, pp. 373-381, 2001.
  26. R. N. Bhattacharya, "Solution growth and electrodeposited CuInSe<sub>2</sub> thin films," *J. Electrochem. Soc.* Vol. 130, pp. 2040-2042, 1983.
  27. T. J. Whang, M. T. Hsieh, Y. C. Kao, and S. J. Lee, "A study of electrodeposition of CuInSe<sub>2</sub> thin films with triethanolamine as the complexing agent," *Appl. Surf. Sci.*, Vol. 255, pp. 4600-4605, 2009.
  28. R. Ugarte, R. Schrebler, R. Cordova, E. A. Dalchiale, and H. Gomez, "Electrodeposition of CuInSe<sub>2</sub> thin films in a glycine acid medium," *Thin Solid Films*, Vol. 340, pp. 117-124, 1999.
  29. F. J. Pern, J. Goral, and R. J. Matson, "Device quality thin films of CuInSe<sub>2</sub> by a one-step electrodeposition process," *Solar Cells*, Vol. 24, pp. 81-90, 1988.
  30. M. Ganchev, J. Kois, M. Kaelin, S. Bereznev, E. Tzvetkova, O. Volobujeva, N. Stratieva, and A. Tiwari, "Preparation of Cu (In,Ga)Se<sub>2</sub> layers by selenization of electrodeposited Cu-In-Ga precursors," *Thin Solid Films*, Vol. 511-512, pp. 325-327, 2006.
  31. M. Kemell, M. Ritala, H. Saloniemi, M. Leskela, T. Sajavaara, and E. Rauhala, "One-step electrodeposition of Cu<sub>2-x</sub>Se and CuInSe<sub>2</sub> thin films by the induced co-deposition mechanism," *J. Electrochem. Soc.*, Vol. 147(3), pp. 1080-1087, 2000.
  32. S. Beyhan, S. Suzer, and F. Kadirgan, "Complexing agent effect on the stoichiometric ratio of the electrochemically prepared CuInSe<sub>2</sub> thin films," *Sol. Energy Mater. Sol. Cells*, Vol. 91, pp. 1922-1926, 2007.
  33. R. N. Bhattacharya, and A. M. Fernandez, "CuIn<sub>1-x</sub>GaxSe<sub>2</sub>-based photovoltaic cells from electrodeposited precursor films," *Sol. Energy Mater. Sol. Cells*. Vol. 76, pp. 331-337, 2003.
  34. C. Sene, M. Estela Calixto, Kevin D. Dobson, and R. W. Birkmire, "Electrodeposition of CuInSe<sub>2</sub> absorber layers from pH buffered and non-buffered sulfate-based solutions," *Thin Solid Films*, Vol. 516, pp. 2188-2194, 2008.
  35. H. Lee, W. Lee, J. Y. Kim, M. J. Ko, K. Kim, K. Seo, D. K. Lee, and H. Kim, "Highly dense and crystalline CuInSe<sub>2</sub> thin films prepared by single bath electrochemical deposition," *Electrochimica Acta*, Vol. 87, pp. 450-456, 2013.