Ordered Vacancy Compound Formation by Controlling Element Redistribution in Molecular-Level Precursor Solution Processed CuInSe2 Thin Films

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It has been reported that the formation of a thin layer of ordered vacancy compound (OVC) on a chalcopyrite absorber layer would provide a high quality p–n junction owing to similarity in their crystal structures as well as a better band alignment for carrier transport in thin film solar cells.2–3 Most studies on the formation of the OVC phase on the chalcopyrite phase have been carried out for vacuum processed Cu(In,Ga)Se2 (CIGS) related thin films. Although the use of high vacuum deposition techniques for the preparation of CIGS absorbers allowed researchers to fabricate thin film solar cells with power conversion efficiencies (PCE) over 20%,6–9 for CIGS thin film solar cells to be more competitive in the photovoltaic market, it will be necessary to reduce processing cost as well as initial investment cost. In the effort of reducing production cost of CIGS solar panels, various kinds of nonvacuum processes have been developed.9–11

Nonvacuum approaches to CIGS layer deposition can be roughly divided into three different categories: electrochemical process, particulate process, and molecular-level precursor solution process.9 The PCE of nonvacuum processed CIGS thin films solar cells have steadily increased.9,10 However, research on the formation of the OVC phase on and/or in chalcopyrite films prepared by nonvacuum processes have not been extensively carried out yet. A better understanding on the formation mechanism of the OVC phase in solution processed CIGS related thin films could provide an opportunity for researchers to improve further performances of the solution processed thin film solar cells.

Here, we report the formation of the OVC phase preferentially on the top surface region of the CuInSe2 (CIS) thin films prepared by a hydrazine solution process. It was also possible to form the OVC phase relatively uniformly through the bulk of CIS films. Although the prepared films are not pure CuInSe2, we here noted the films as CuInSe2 because the films are devoid of sulfur, less than 5 at. %, despite the addition of excess sulfur to the precursor solutions. The hydrazine solution process used in this work has demonstrated the highest PCE among the molecular-level precursor solution processed thin film solar cells.12 In a vacuum process, each atomic flux reaching to substrates can be controlled in real time, so that desired phases can be relatively easily formed in desired regions. In contrast, those works are relatively difficult in solution processes. We here show that adjustment of the degree of decomposition of molecular precursors during film preparation will make those works possible even in solution processes.

CIS thin films were prepared by spin-coating CIS-precursor solutions, and then present phases in the prepared films were identified using Raman spectroscopy (Figure 1). Preparation of the precursor solutions and the CIS thin films were performed inside a N2 filled glovebox. All of the precursor solutions were prepared by dissolving desired powders into hydrazine. Caution: hydrazine is highly toxic and should be handled with appropriate protecting equipment to prevent contact with either the vapors or liquid. The CIS-precursor solutions were prepared by simply combining Cu-precursor solutions and In-precursor solutions. The Cu-precursor solutions were prepared by simply dissolving Cu2S and sulfur powder into hydrazine. The In-precursor solutions were prepared by dissolving In2Se3 and Se powder with equal molar ratios into hydrazine. To dissolve completely the employed powders, Cu- and In-precursor solutions were stirred for several days. CIS thin films were deposited on Mo-coated soda lime glass substrates by spin-casting the prepared CIS-precursor solutions at a spin speed of 3000 rpm for 30 s. Each CIS layer thickness

![Figure 1. Process flow for the preparation and the Raman characterization of CuInSe2 thin films.](image-url)
was about 150 nm. To prepare thicker CIS films, the coating step was repeated multiple times. Between each coating step, the samples were annealed on a preheated hot plate at a temperature of 220–290 °C for a few minutes, and finally annealed on a hot plate at a temperature of 400 °C for 30 min.

Raman analysis was performed on the prepared CIS thin films to identify the present phases in a confocal backscattering configuration at room temperature with unpolarized light using a Renishaw inVia Raman system equipped with a 514.5 nm Ar laser. The laser beam size was approximately 2 μm. Penetration depth into CIS films of the Ar laser (514.5 nm) used in this Raman spectroscopy is estimated to be approximately 100 nm. In other words, depth resolution of this measurement is about 100 nm.

Raman spectroscopy has been known to be one of the best tools to identify clearly both the chalcopyrite phase and OVC phase simultaneously. The A1-mode is corresponding to selenium atom vibration with respect to their neighboring atoms. In the chalcopyrite CIS phase, each Se atom is bonded with two indium atoms and two copper atoms. In the OVC phase, some fraction of copper atoms is replaced by vacancies and indium atoms, so that the A1-mode in the OVC phase exhibits a lower value of corresponding peak position compared to that in the CIS chalcopyrite phase.

Raman spectra were obtained from the top surface, the back surface, and the cross section of a CIS thin film to identify present phases at each position (Figure 2). To probe the present phase at the back surface, the film was mechanically exfoliated and flipped over for Raman spectroscopic analysis. A spectrum obtained from the top surface showed two distinct peaks located at 175 and 152 cm⁻¹ coming from the CIS phase and OVC phase, respectively. The peak height ratio of OVC/CIS was approximately 0.55. In contrast, a Raman spectrum obtained from the bottom surface showed a strong CIS peak but a negligibly weak OVC peak. To explore present phases in the bulk of CIS films, we obtained Raman spectra from the cross section of the film. It should be noted that Raman spectrum obtained from the cross section represents the microstructural properties of whole bulk of the film because Ar laser beam size (~2 μm) fully covers the thickness of the film (~1 μm). Raman spectrum obtained from the cross section of the film also showed a strong CIS peak but a negligibly weak OVC peak, similar to the spectrum obtained from the back surface. On the basis of the measured three Raman spectra, we reasonably reach a temporary conclusion that the OVC phase is formed preferentially in the topmost layer of the prepared CIS films.

To understand how the OVC phase is present preferentially in the topmost layer of the solution processed multilayered CIS thin films, we traced the intensity of the OVC phase peak obtained from the top surface of the films with different number of layers (Figure 3). With increasing the number of coating layers from two to eight, the peak height ratio of OVC/CIS was almost linearly increased to the number of layers from 0.16 to 0.61, indicating that the content of the OVC phase on the top surface layer was gradually increased. Because the OVC phase has more indium content than the CIS phase, it is thus evident that indium content on the top surface layer was progressively increased with repeating spin-casting of CIS-precursor solutions.

A potential mechanism for this observation is as follows. \[\text{[Cu}_6\text{S}_4\text{]}^{2-} \text{ and [In}_2\text{Se}_4\text{]}^{2-}\] are two major molecular complexes in hydrazine CIS-precursor solutions. \[\text{[Cu}_6\text{S}_4\text{]}^{3-}\] ions convert to Cu-S sheets by losing sulfur while drying at room temperature and completely convert insoluble Cu-S phase at temperatures below 120 °C. In contrast, readily soluble \[\text{[In}_2\text{Se}_4\text{]}^{2-}\] related species are fairly thermally stable even after casted on substrates, so higher temperature annealing above 350 °C is required to convert them completely to an insoluble solid phase. Note that the samples were annealed at temperature in the range of 220–290 °C between each coating step. By considering the thermal stability of two major complexes, \[\text{[Cu}_6\text{S}_4\text{]}^{3-}\] and \[\text{[In}_2\text{Se}_4\text{]}^{2-}\], and annealing temperature between each coating step, casting CIS-precursor solutions for the deposition of the following upper layer partially redissolves \[\text{[In}_2\text{Se}_4\text{]}^{2-}\] related species from the under layer. As a result, redissolved indium species are redeposited in the following upper layer, which then becomes more indium rich than the casted CIS-precursor solution as well as the under

Figure 2. Raman spectra obtained from the top surface, the back surface, and the cross section of a CuInSe_2 thin film. Each position was marked on the cross-sectional scanning electron microscopy image of a CuInSe_2 thin film.

Figure 3. (a) Raman spectra and (b) OVC/CIS peak height ratio obtained from the top surface of CuInSe_2 thin films with different number of layers.
layer. By repeating this procedure, indium content is gradually increased in the topmost layer. This high indium content thus causes the formation of the OVC phase preferentially in the topmost layer.

On the basis of our suggested mechanism for this experimental observation, high temperature annealing above 350 °C between each coating step will completely convert indium precursor complexes to an insoluble solid phase. In other words, redissolving indium complex species will be highly suppressed by thermal annealing at temperatures above 350 °C. Thus, an OVC peak will not be significant even in the topmost layer.

Designed experimental work was thus performed, in which the annealing temperature between each coating step was simply raised up to 390 °C. Figure 4 shows Raman signals obtained from the top surface and the back surface of the CuInSe2 film that was prepared by raising soft annealing temperature between each coating step to 390 °C to convert completely indium precursor species to an insoluble solid phase.

Figure 4. Raman spectra obtained from the top surface and the back surface of the CuInSe2 film that was prepared by raising soft annealing temperature between each coating step to 390 °C to convert completely indium precursor species to an insoluble solid phase.

In summary, we investigate the mechanism of OVC phase formation in the CIS films prepared by a hydrazine solution process, which has demonstrated the highest PCE thin film solar cells among molecular-level precursor solution processes. By selectively redissolving indium species during casting precursor solutions for the following upper layer, the OVC phase relatively uniformly through the back surface. We assume that the OVC phase is relatively suppressed (compare to Figure 2) with no significant difference from that obtained from the back surface. We assume that the OVC phase is relatively uniformly distributed through this film prepared in this designed experiment. It has been recently reported that the OVC phase exists deep into the bulk of a high-efficiency CIGS absorber prepared by a three-stage vacuum process. This work implies that thermal behaviors of molecular precursors are responsible for element redistribution and phase formation in desired regions.

In summary, we investigate the mechanism of OVC phase formation in the CIS films prepared by a hydrazine solution process, which has demonstrated the highest PCE thin film solar cells among molecular-level precursor solution processes. By selectively redissolving indium species during casting precursor solutions for the following upper layer, the OVC phase was formed preferentially in the topmost layer in the CIS films. In addition, by adjusting the annealing temperature between each coating step, we were able to form the OVC phase relatively uniformly through the films. Intentional variation of stoichiometry in precursors for each layer deposition as well as higher resolution analysis techniques will be necessary to clarify additionally more details of how the OVC and CIS phases are arranged and their effects on the performances of thin film solar cells. We anticipate that this work can be applied to water and/or alcohol-based nontoxic molecular-level precursor solution processes by understanding the thermal properties of molecular complexes present in each solution.

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C.-H.C. conceived the idea, wrote the paper, and did the experiment. K.H.H., D.W.L., and J.H.Y. did interpretation of data and wrote the paper. Y.Y. conceived the idea and guided research.

Notes
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[REFERENCES]


(12) Todorov, T. K.; Gunawan, O.; Gokmen, T.; Mitzi, D. B. Solution-processed Cu(In,Ga)(S,Se)$_2$ absorber yielding a 15.2% efficient solar cell. Prog. Photovoltaics 2013, 21, 82.


