Secondary Phase Formation in (Ag,Cu)(In,Ga)Se₂ Thin Films Grown by Three-stage Co-evaporation

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Abstract

(Ag,Cu)(In,Ga)Se₂ thin films deposited by a three-stage co-evaporation process have shown potential as mid- and wide-bandgap absorber materials for solar cell devices. Further growth optimization requires a thorough understanding of secondary phases formed in addition to the primary chalcopyrite phase, during the group-I rich growth near the end of the second stage. In this study, we investigate how the composition ratio Ag/(Ag+Cu) controls the formation of the secondary phases containing Ag, Cu and Se. Group-I rich [composition ratio (Ag+Cu)/(In+Ga)>1] ACIGS films with varying silver content—Ag/(Ag+Cu)=0, 0.1 and 0.5—are grown until the end of the second stage of three-stage processes. Secondary phases are found to locate near film surfaces. However, they intermix with the chalcopyrite phase in the surface layer when Ag/(Ag+Cu)>0, while they form a separate layer if no Ag is alloyed. The crystal structures of the secondary phases shifts along the Cu₂Se - Ag₂Se pseudo-binary tie-line as Ag/(Ag+Cu) increases. Concurrently, the film surfaces become smoother with reduced facets and voids, the accumulation of sodium is suppressed, and both the degree of In and Ga gradient and the film emissivity are reduced, all of which affect the subsequent deposition process and final solar device performance.

Keywords: Ag-Cu-Se secondary phases, (Ag,Cu)(In,Ga)Se₂, three-stage co-evaporation

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1. Introduction

Thin-film (Ag,Cu)(In,Ga)Se₂ (ACIGS) has been studied for its potential in photovoltaics, with direct comparison to one of the successful thin-film absorbers—Cu(In,Ga)Se₂ (CIGS) [1–5]. It was hypothesized that its reduced melting temperature, as compared to CIGS, may reduce crystal defects related to opto-electrical properties of ACIGS films grown at the same temperature [6]. Co-evaporated ACIGS thin-film solar cells have shown evidence of enhanced grain size and reduced structural disorder which was indicated by smaller Urbach energy [5, 7]. Ag alloying also increases the bandgap E_g of ACIGS [8]. Resulting improvement in device performance has been demonstrated by comparing ACIGS and CIGS devices with similar bandgap, especially with wide bandgap $E_g \geq 1.3$ eV, and 19.9% conversion efficiency has been achieved at $E_g = 1.2$ eV [1, 2, 9].

To deposit CIGS thin films for high-efficiency solar cells, the three-stage co-evaporation process has been a common method [10–12]. This deposition process features a first stage with In+Ga+Se deposition followed by a second stage with Cu+Se and concluded by a third stage of In+Ga+Se. Films undergo a critical transition from Cu poor [$\text{Cu}/(\text{In}+\text{Ga}) < 1$] to Cu rich [$\text{Cu}/(\text{In}+\text{Ga}) > 1$] during the second stage when Cu is added to the precursor containing In and Ga. A second but reverse transition occurs during the third stage when the overall composition becomes Cu poor again under the In+Ga+Se flux.

A number of studies have characterized the effects of the CIGS Cu rich growth. It has been evidenced the phase transition during CIGS film growth follows the Cu₂Se–(In,Ga)₂Se₃ pseudo-binary tie-line [13–16]. The extent of the Cu rich composition [excess Cu beyond what needed to reach $\text{Cu}/(\text{In}+\text{Ga})=1$] in the second-stage was reported to affect the surface roughness of the final CIGS films, which eventually reduces the CdS/CIGS junction quality when it becomes too rough [17]. Regions of segregated Cu_{2–x}Se phase have been detected and are thought to be responsible for the crevices observed in some CIGS films [18–20]. Formation of a descending Ga/(In+Ga) composition gradient from the back to the front surface of CIGS films during the second stage was also reported. This contributes to the commonly observed Ga/(In+Ga) notch shape profiles in CIGS films deposited by a complete three-stage process [15, 21, 22].

The deposition of ACIGS thin films has been successfully demonstrated using the three-stage process [3, 5]. During the second stage, once ACIGS films pass stoichiometry, they are also

expected to undergo group-I rich growth $[(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})>1]$, and form mixture of the chalcopyrite phase and Ag-Cu-Se compounds, or the secondary phases. ACIGS films, with different $\text{Ag}/(\text{Ag}+\text{Cu})$ and similar $\text{Ga}/(\text{In}+\text{Ga})$ composition ratios, were deposited following the three-stage process, however only until the end of the second stage at which the films are group-I rich. We show that, analogous to CIGS, ACIGS forms Ag-Cu-Se secondary phases once chalcopyrite ACIGS reaches stoichiometry. We will present: (1) the location of secondary phases in the films and how their distribution is affected by $\text{Ag}/(\text{Ag}+\text{Cu})$, (2) the crystal structures of the secondary phases, also determined by $\text{Ag}/(\text{Ag}+\text{Cu})$, and (3) the material property changes induced by these phases including film morphology, sodium accumulation, In and Ga gradients and film emissivity.

2. Experimental Section

ACIGS thin films were deposited in vacuum onto soda-lime glass substrates coated with a 700-nm thick sputtered Mo back contact. The ACIGS deposition followed a three-stage co-evaporation process [5] during which In and Ga were delivered in the first stage, followed by Cu and Ag during the second stage, however no third stage was included. This deposition procedure was intended to render films group-I rich with the secondary phases formed. During the deposition process, Se was evaporated at constant flux and its over-pressure was maintained at a molar flux rate 8 to 10 times higher than the total flux of all the metal vapors. The substrate temperature was $T_{\text{ss}}=350^\circ\text{C}$ during the first stage and $T_{\text{ss}}=580^\circ\text{C}$ during the second. During the deposition, the film emissivity was indirectly measured by a thermocouple inserted between substrates and their heater [23], so the films' stoichiometry was observed. The deposition time for the first and second stages was 30 and 45 minutes respectively, and was pre-programmed into the process control system before each deposition run, which unfortunately couldn't be adjusted once the deposition started. Therefore no end-point-detection method was used to change the deposition time for the second stage, which resulted in different $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})$ composition ratio in films. [24] However, in all films sufficient $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})>1$ or group-I richness was ensured by the long enough deposition time for the second stage. In this work, three group-I rich ACIGS films (referred as A, B, C) were grown with different $\text{Ag}/(\text{Ag}+\text{Cu})$ composition ratio and nominally the same $\text{Ga}/(\text{Ga}+\text{In})$ for each sample. To better identify crystal

phases, three additional pure Ag-Cu-Se films (referred as D, E, F) with similar Ag/(Ag+Cu) composition ratios were deposited only during the second stage of a three-stage process.

X-ray fluorescence (XRF) was used to determine the average elemental composition of the films, since the energetic x-rays penetrate through the whole films. Energy dispersive x-ray spectroscopy (EDS), stimulated by an electron source of 20 kV acceleration voltage with sampling depth of 0.3 - 0.5 μm in ACIGS films, was also used to determine the elemental composition. Compositions were measured by EDS from both the front and back surfaces of films, before and after they were peeled off at the ACIGS/Mo interface. Composition depth profiles in films were measured by secondary ion mass spectroscopy (SIMS), performed by Evans Analytical Group. The morphologies of both front surfaces and cross sections of films were examined by scanning electron microscopy (SEM) with cross-sectional images taken using an in-lens secondary electron detector located inside the electron column of the microscope. The in-lens detector enhances the secondary electron collection and can achieve high contrast from negative charging of samples (charging contrast), which otherwise would be obscured by topographical contrast. Composition mapping was measured on a JEOL 2010F transmission electron microscope (TEM) under the scanning transmission electron microscope (STEM) mode. Generated by an electron beam at 200 kV acceleration voltage, energy dispersive x-ray spectroscopy (EDS) measurements were acquired by a EDAX Si-Li x-ray detector at each sampling point, as the electron beam rastered across the sample. Elemental distribution profiles were created by reconstructing the peak areas of the Ag-L, Cu-K, In-L, Ga-K, Se-L Mo-L and Pt-L peaks at each location. The sample lamellae were prepared by focused ion beam (FIB) in a Zeiss Auriga 60 Crossbeam scanning electron microscope (SEM). During the preparation, about 1 μm thick Pt layer was deposited on the film front surfaces as a protection from ion beam damage. The lamellae were polished by FIB to ≤ 100 nm thick, therefore the spatial resolution of the composition mapping measured by EDS is controlled by the beam size of the electron source and the step size of the scans, without substantial lateral spread of the excitation volume. The crystal structures were studied by glancing incidence x-ray diffraction (GIXRD) at incident angle of $\Omega = 0.5, 1, 2, 4$ and 8° to probe the Ag-Cu-Se compound from the surfaces to the bulks of the films. In GIXRD, Cu x-ray source was used, and a scan of the diffraction was taken in the range $10^\circ \leq 2\theta \leq 70^\circ$ with step size $\Delta 2\theta = 0.05^\circ/\text{step}$ and scan speed $0.5^\circ/\text{min}$. Rietveld refinement on

unit cells was performed in HighScore Plus ®, based on the crystallographic information files (CIF) from ICSD and ICDD databases [25, 26], as well as references [27–32]. Possible systematic offsets in 2θ of each patterns were identified using the Mo peaks based on its powder diffraction file. A March-Dollase model was used to refine the preferred orientation [33, 34].

3. Results and Discussion

3.1. Existence and Location of Secondary Phases

Suggested by the $\text{Ag}_2\text{Se-In}_2\text{Se}_3$, $\text{Cu}_2\text{Se-In}_2\text{Se}_3$, $\text{Ag}_2\text{Se-Ga}_2\text{Se}_3$ and $\text{Cu}_2\text{Se-Ga}_2\text{Se}_3$ pseudo-binary phase diagrams [13, 35–39], one would expect secondary phases—a compound containing only Ag, Cu and Se—to form in a ACIGS film grown by the three-stage process, after the film becomes group-I rich, i.e., $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga}) > 1$. Such composition can be achieved at the end of the second stage. In such films, the existence and the location of the secondary phases were revealed by composition depth profiling and mapping, and their dependence on Ag content is discussed.

Three ACIGS films labeled as A, B and C were deposited with varying Ag but fixed Ga concentration, following the three-stage co-evaporation process but only until the end of the second stage. Table 1 shows their elemental composition and ratios measured by XRF. The composition ratio $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})$ is greater than unity in all three films, indicating their group-I richness. The slight difference in $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})$ of each sample was a result of the unavoidable change in flux during each deposition process, given the same deposition time. All samples are sufficiently group-I rich to characterize the secondary phases and to explore the effect of $\text{Ag}/(\text{Ag}+\text{Cu})$ on their formation. Therefore, $\text{Ag}/(\text{Ag}+\text{Cu})$ was intentionally varied among films A, B and C. The group-I rich ACIGS films were also deposited with nominally the same $\text{Ga}/(\text{In}+\text{Ga}) \approx 0.55$ since an earlier study has shown it has no effect on the secondary phases [40].

To locate the secondary phases, elemental depth profiles of the CIGS (film A) and ACIGS (film C) films were measured by secondary ion mass spectroscopy (SIMS). The $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})$ is shown as a function of depth in Figure 1, with profiles plotted from the films' front to the back surfaces. Both samples contain surface layers with $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga}) > 1$, and stoichiometric $[(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})=1]$ bulk. This is consistent with the hypothesis that once chalcopyrite CIGS and ACIGS phase reach stoichiometry, Cu-Se and Ag-Cu-Se compounds will form as secondary

Table 1: Elemental composition and ratios of group-I rich ACIGS films A, B and C, grown by only the first and second stages of a three-stage co-evaporation. Compositions were measured by XRF on the front sides of films.

Film	Ag [at.%]	Cu [at.%]	In [at.%]	Ga [at.%]	Se [at.%]	Ag / (Ag+Cu)	Ga / (In+Ga)	(Ag+Cu) / (In+Ga)
A	0.0	33.1	7.5	12.0	47.3	0.00	0.61	1.70
B	2.2	32.9	7.5	9.6	47.8	0.06	0.56	2.05
C	15.0	15.8	9.7	11.8	47.7	0.49	0.55	1.43

phases. The surface layer in both film A and C is approximately $0.5 \mu\text{m}$ thick and contains the secondary phases. A CIGS film with $\text{Cu}/(\text{In}+\text{Ga}) = 1.4$, matching sample C, would have the same surface structure only in a thinner layer. Therefore the difference in $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})$ of the two films isn't believed to have effect on how the Ag-Cu-Se secondary phases are distributed with respect to the chalcopyrite phase.

The inset in Figure 1 shows the Ag and Cu composition profiles. In the CIGS film, higher Cu content is observed near the front surface, as a result of the segregation of the Cu-Se secondary phases. In the ACIGS film, however, higher Ag but lower Cu is observed near the surface. In addition to being group-I rich, the ACIGS film surface contains higher $\text{Ag}/(\text{Ag}+\text{Cu})$ than the chalcopyrite ACIGS bulk. Given the deposition process during the second stage in which Ag and Cu are incorporated into the $(\text{In},\text{Ga})_2\text{Se}_3$ precursor from the film front surfaces, this observation suggests that Cu preferentially reacts with $(\text{In},\text{Ga})_2\text{Se}_3$, considering the similar or higher diffusion coefficient of Ag than Cu [41, 42]. This observation is also consistent with the Ag segregation seen in the three-stage growth of $\text{Ag}(\text{In},\text{Ga})\text{Se}_2$ [43] and of ACIGS in which a $\text{Ag}/(\text{Ag}+\text{Cu})$ gradient reaches its maximum in the middle of the film [5].

To distinguish whether the secondary phases are mixed with the chalcopyrite phase near the film surfaces, or they form a separated layer, the Ag-Cu-Se containing grains were located at a microscopic scale. To do so, elemental composition mapping near the surfaces of the CIGS (film A) and ACIGS (film C) films was measured by energy dispersive x-ray spectroscopy (EDS) using scanning transmission electron microscope (STEM) on thin lamellae of film cross sections. Figure 2 shows the Cu, In, Ga and Se distribution, and the corresponding high angle annular dark field (HAADF) image of the CIGS sample. It's observed that some grains at the surface contain

Figure 1: The $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})$ profiles in CIGS (film A) and ACIGS (film C) films. Profiles were measured by SIMS from front surface (left) to Mo interface (right). Inset shows the Ag and Cu atomic percentage in each film, respectively.

Figure 2: Elemental distribution near the surface of CIGS film A, measured by EDS in STEM. The same location was imaged by the HAADF detector, with the film front surface oriented at the top of the images.

Figure 3: Elemental distribution near the surface of ACIGS film C, measured by EDS in STEM. The same location was imaged by the HAADF detector, with the film front surface oriented at the top of the images.

higher Cu but almost no In and Ga, which suggests these grains are Cu-Se compounds only. After several other locations near the CIGS film surface were examined, it was concluded that Cu-Se grains cover $\geq 80\%$ of the surface. The same composition mapping on the ACIGS film is shown in Figure 3. Since ACIGS films typically have large and columnar grains [5], only one large grain and a small grain at the surface are observed in the dark field image. The composition map shows this small grain has higher Ag and Cu than the rest of the region, with no Ga and little In. It is believed the weak but non-zero In signal from this grain is a measurement artifact as a result of the overlapping Ag- $L_{\beta 1}$ and In- L_{α} peaks. This Ag-Cu-Se grain on film surface was only found at this location, with no Ag-Cu-Se grains found at other locations on this ACIGS lamella that has been scrutinized. Most of the film was covered by ACIGS phase instead of Ag-Cu-Se secondary phases, in contrast to the CIGS film. This accounts for the almost an order of magnitude lower $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})$ near the ACIGS film surface. Although the small grain seems to contradict the $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})$ measured by SIMS near film C surface, it's necessary to point out the SIMS measurement averages between the secondary-phase and chalcopyrite grains in the surface layer over an approximately 1 mm^2 area. Since the secondary phase grains have no In or Ga and the chalcopyrite grains have $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})=1$, even a small secondary phase grain can result in average $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})>1$. Meanwhile, a $\sim 25 \text{ nm}$ thick layer at the very surface of the film has higher Ag signal which could be also associated with Ag-Cu-Se, although this wasn't observed at other sites that were examined.

3.2. Crystalline Phases

X-ray diffraction from films A, B and C was measured at grazing incident angles $\Omega = 0.5^\circ, 1^\circ, 2^\circ, 4^\circ$ and 8° to study the depth dependence of the crystal structures of the Ag-Cu-Se secondary phases. Figure 4 shows the diffractograms measured on film C as an example, with the intensity of the chalcopyrite (112) peaks normalized to unity. It is clear the relative peak intensity from the secondary phases decreases almost by half, as the incident angle and therefore the penetration depth increase. This confirms the secondary phases only exist near the film surface, given that the peak intensity is proportional to the measured volume. At $\Omega = 0.5^\circ$, diffractograms measured on films A, B and C are shown in Figure 5. It demonstrates that different Ag/(Ag+Cu) in each film has resulted in different crystal structures in the secondary phases. However, even at this angle with penetration depth of 80-200 nm, diffraction peaks from the chalcopyrite phase still appear (as referred to the $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ powder diffraction pattern, ICDD card 00-040-1488 [25]), and they overlap with some of the peaks from the secondary phases due to their similar crystal structures. One diffraction peak from film C indicates the existence of Mo, although Mo layer is out of the probing depth at $\Omega = 0.5^\circ$. This may be attributed to the fact that the Mo near the edges of the substrate was not completely covered during ACIGS deposition.

To overcome the uncertainty created by overlapping diffraction peaks in identifying the secondary phase structures, films D, E and F containing pure Ag-Cu-Se compounds were deposited on Mo coated glass substrates just following the second stage growth procedure of the three-stage process. Table 2 shows the composition and Ag/(Ag+Cu) measured on films D, E and F by XRF. Since the secondary phases exist only near the surfaces of films A, B and C, and contain higher Ag/(Ag+Cu) than in the bulk chalcopyrite phase, films D, E and F were grown with composition similar to the near surface regions of films A, B and C, respectively (see Supporting Information). Since films D, E and F were grown with constant Ag and Cu flux, it was expected to form homogeneous films without variation in composition or phases. Unintentional In and Ga, less than 2.5%, is seen in these films, because of the residual In and Ga flux existing in the second stage deposition due to the lack of individual source shutters in the system. However, this is not believed to impact the crystal structure of the Ag-Cu-Se compounds and the subsequent phase identification.

When symmetrical XRD was measured on films D, E and F (data not shown), fewer diffrac-

Figure 4: Comparison of the normalized diffractograms of film C measured at various incident angles from $\Omega = 0.5^\circ$ to 8° . The peaks from the chalcopyrite phase and Mo are labeled. The unlabeled peaks are from the secondary phases. The highest intensity of the chalcopyrite (112) peak near 26.5° from each diffractogram is normalized to 1.

Table 2: Elemental composition and Ag/(Ag+Cu) in pure Ag-Cu-Se films D, E and F deposited only during the second stage of a three-stage process. Compositions were measured by XRF on the film front surfaces.

Film	Ag [at.%]	Cu [at.%]	In [at.%]	Ga [at.%]	Se [at.%]	Ag / (Ag+Cu)
D	0.0	60.3	1.5	1.1	37.1	0.00
E	16.4	43.2	1.4	2.0	36.9	0.28
F	37.8	22.5	2.0	2.4	35.4	0.63

Figure 5: Diffractograms of group-I rich ACIGS films A, B and C measured by GIXRD at incident angle $\Omega = 0.5^\circ$. Comparison of films A, B and C shows different crystalline phases exist in each film. Listed powder diffraction patterns is $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ (ICDD card 00-040-1488) [25], and a peak at 40.5° is attributed to Mo exposed at the sample edge. The unlabeled peaks belong to the secondary phases, however aren't phase identified yet due to their overlapping with chalcopyrite phase. Crystal structure of the secondary phases based on x-ray diffraction will be analyzed in the next section with films D, E and F. The intensities of the X-ray diffraction are normalized and in linear scale.

Table 3: Identified crystal structures in the secondary phases. The phases are identified from the pure Ag-Cu-Se films D, E and F, using Rietveld refinement, and their diffraction peaks are shown in Figure 6.

Label	Formula	Temp. Range	Space Group	a [Å]	b [Å]	c [Å]	In Film	Ref.
a	Cu_{2-x}Se	high temp.	Fm-3m (225)	5.732	5.732	5.732	D, E	[27]
b	Cu_2Se	room temp.	C2/c (15)	7.031	12.329	26.942	D, E	[28]
c	$(\text{Ag,Cu})_{2-x}\text{Se}$	high temp.	Fm-3m (225)	5.666	5.666	5.666	E, F	[29]
d	AgCuSe	room temp.	Pmmn (59)	4.240	3.947	6.123	E, F	[29]
e	Ag_2Se	room temp.	P2 ₁ 2 ₁ 2 ₁ (19)	4.329	7.037	7.753	F	[30]
m	Mo	n/a	Im-3m (229)	3.147	3.147	3.147	D, E, F	[32]

tion peaks from each film were observed, compared to corresponding ACIGS films A, B and C in Figure 5. An asymmetric scan on films D, E and F at incident angle $\Omega = 8^\circ$, as shown in Figure 6, however, revealed the same set of peaks as in films A, B and C. It's possible the films were grown with preferred orientation. Diffractograms of films D, E and F at different incident angles from $\Omega = 0.5^\circ$ to 8° were also compared (not shown), but no composition gradient was observed. By comparing diffraction peaks from films D, E and F with films A, B and C, respectively, it confirms the same crystal structures exist in the secondary phases from the group-I rich ACIGS films as in the corresponding pure Ag-Cu-Se films. Crystal phases in films D, E and F are identified using Rietveld refinement and their corresponding diffraction peaks are labeled in figure 6, with their crystal structures summarized in Table 3. It clearly shows that film D with $\text{Ag}/(\text{Ag}+\text{Cu})=0$ contains the high temperature Cu_{2-x}Se and the room temperature Cu_2Se phases. Film E with $\text{Ag}/(\text{Ag}+\text{Cu})=0.28$ contains both the Cu_2Se phases, the high temperature $(\text{Ag,Cu})_{2-x}\text{Se}$ and the room temperature AgCuSe phases. Film F with $\text{Ag}/(\text{Ag}+\text{Cu})=0.63$ contains the $(\text{Ag,Cu})_{2-x}\text{Se}$, the AgCuSe , and the room temperature Ag_2Se phases. Nevertheless, the existence of phases under different $\text{Ag}/(\text{Ag}+\text{Cu})$ is consistent with the Ag_2Se and Cu_2Se pseudobinary phase diagram [44, 45]. The different phase formation in the Ag-Cu-Se compounds as a result of $\text{Ag}/(\text{Ag}+\text{Cu})$ ratio has affected the subsequent reaction with In and Ga at the beginning of the third stage, as evidenced by the series of changes in the film emissivity [40].

Figure 6: Diffractograms of pure Ag-Cu-Se films D, E and F measured by GIXRD at incident angle $\Omega = 8^\circ$. Comparison of films D, E and F shows different crystalline phases exist in each film, as Ag content varies. Diffraction peaks are labeled according to the identified phases which are listed in Table 3 [25]. The intensities of the diffractograms are in logarithmic scale.

Figure 7: Plan-view SEM images of all films A to F as labeled on images. Difference in film surface morphology is seen as Ag content in films varies. Images were all taken at $30,000\times$ magnification.

3.3. Effect of Secondary Phases on Film Growth

The formation of the secondary phases has strong effect on the morphology, the sodium concentration, the In and Ga composition gradients and the emissivity of the ACIGS films, which is controlled by Ag content.

3.3.1. Film Morphology

To characterize surface morphology, plan-view SEM images of all the films are compared in Figure 7. From A to B to C, as well as from D to E to F, the surface becomes smoother and contains fewer facets and voids as the $\text{Ag}/(\text{Ag}+\text{Cu})$ ratio increases. This is because of the changes not only in (1) the film surfaces content from almost pure secondary phases (Cu-Se) to a mixture of secondary phases (Ag-Cu-Se) and chalcopyrite, but also in (2) the surface morphology of the secondary phases themselves, as demonstrated by the change from D to E to F. According to the pseudobinary and ternary phase diagrams, the Cu-Se and Ag-Se compounds in films D, E and F should all contain liquid phase(s) at the growth temperature of 580°C [46–48]. However, the portion of the liquid phase(s) in each mixture may differ depending on the $\text{Ag}/(\text{Ag}+\text{Cu})$. And the facets and voids can also result from different cooling characteristics of each phase. On the other hand, the surface grain size changes by a factor of two to three with the increase of Ag in the films, which is consistent with the larger grain size in ACIGS than CIGS as reported earlier [5].

The film cross sections were examined, with the aim to observe the layered structure as observed in the TEM composition mapping. SEM cross-section images of each fractured film, shown in Figure 8, were recorded using an in-lens secondary electron detector in the SEM to capture contrasts created by electron charging in addition to morphology contrast. Differences in thickness are due to the different growth time as indicated in Table 1 and 2. A lack of layered structure in films A, B and C is attributed to the similarity between the secondary phases and

Figure 8: Cross-section SEM images of fractured films A to F as labeled on images. Images were all taken at 30,000 $\times$ magnification using an in-lens secondary electron detector.

chalcopyrite in both (1) cross-section morphology, as seen in the comparison of A and D, B and E, C and F, and in (2) resistivity [23, 49, 50]. The increase in grain size as Ag/(Ag+Cu) increases from A to B and C is consistent with the plan-view images, and the cross-section morphology agrees with that in TEM mapping and HAADF images.

3.3.2. Sodium Accumulation

Sodium (Na) typically diffuses into CIGS and ACIGS films as an impurity, from the commonly used soda-lime glass substrates during the film deposition. It is widely observed that the incorporation of Na into CIGS and ACIGS films improves the electronic performance of corresponding solar devices [51–54].

Figure 9 compares the Na depth profiles in the CIGS (film A) and the ACIGS (film C) films, plotted from their front surfaces to back surface. Both films show local maximum Na concentration near the transition point from stoichiometric $[(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})=1]$ to group-I rich $[(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})>1]$ regions, as indicated by the overlaid $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})$ profiles. This Na segregation is consistent with what was observed earlier that Na peaks appear in the middle of ACIGS and CIGS films deposited by a complete three-stage process [5]. And it verifies the earlier observation that the Na segregation is stronger in CIGS than in ACIGS. One possible hypothesis to explain this is the larger amount of secondary phases on the CIGS film surface than on ACIGS surface, as indicated by the TEM mapping. And Na has been speculated to react with Ag-Cu-Se and Cu-Se secondary phases to form ternary $\text{Na}_x\text{Cu}_y\text{Se}_z$ or $\text{Na}_x\text{Ag}_y\text{Se}_z$ [55, 56]. Another possibility is the facets and voids in the Cu-Se secondary phases on the CIGS surface provide more grain boundaries at which Na primarily segregates [57]. However, neither of these hypotheses can explain why the Na only segregates locally at the transition point from the stoichiometric to the group-I rich regions, instead of the whole surface layer which contains the secondary phases.

Figure 9: Comparison of Na concentration profiles in CIGS (film A) and ACIGS (film C) films. Profiles were measured by SIMS from film front surface (left) to Mo interface (right). Plotted together are the $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})$ composition profiles. The Na maxima are near $0.5 \mu\text{m}$ depth where the films transition from stoichiometric chalcopyrite phase to secondary phases.

3.3.3. In and Ga Profiles

In and Ga depth profiles control the bandgap gradients in CIGS and ACIGS films, and the bandgap gradient has been widely studied by experiments and device simulations to show its impact on the device performance [9, 58–62]. Figure 10 compares the In and Ga depth profiles in the CIGS (film A) and ACIGS (film C) films. The In and Ga gradients are comparable in the bulk of both films, but in the CIGS film they decrease abruptly to ~ 1 at.% within $0.3 - 0.5 \mu\text{m}$ depth from the surface. This is consistent with the surface layer mostly containing Cu-Se secondary phases in the CIGS film. In contrast, in the ACIGS film the In and Ga gradually decrease to 5 at.% at the front surface, which is consistent with the co-existing chalcopyrite and Ag-Cu-Se secondary phases in the surface layer.

As shown in Figure 11, $\text{Ga}/(\text{In}+\text{Ga})$ in both films has an ascending gradient toward the back surface, beginning from its minimum at the point where the growth of the stoichiometric chalcopyrite phase stops, as indicated by the $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga})$ profiles. This confirms the $\text{Ga}/(\text{In}+\text{Ga})$ gradient formation is associated with intermixing of group I and III elements that causes preferential reaction and/or diffusion. The different distribution of the secondary phases in the surface layers of group-I rich ACIGS and CIGS films will affect the slope of the $\text{Ga}/(\text{In}+\text{Ga})$ gradients if continue to form in the third stage. Because if the films were allowed to continue their growth in the third stage, In and Ga would react almost only with the Cu-Se compounds on the CIGS surface, and result in $\text{Ga}/(\text{In}+\text{Ga})$ comparable to the delivering flux. However, in the ACIGS film growth, In and Ga would incorporate mostly into the existing ACIGS grains which cover most of the ACIGS film surface, and only gradually increase the $\text{Ga}/(\text{In}+\text{Ga})$. Therefore, a steeper $\text{Ga}/(\text{In}+\text{Ga})$ gradient from its minimum to the film surface has been typically observed in CIGS films than in ACIGS films, if they are deposited by a complete three-stage process [5].

3.3.4. Surface Emissivity

The difference in the secondary phases also affects the emissivity of the group-I rich ACIGS and CIGS films. During a three-stage deposition process, the film emissivity is indirectly measured by a floating thermocouple inserted between substrates and their heater, as described in Ref. [23]. According to Stefan-Boltzmann law, in vacuum with radiation essentially the only method of heat transfer, the change in substrate heating power is proportional to the change in the film emissivity, when the substrate temperature is constant. So the floating thermocouple

Figure 10: Comparison of In and Ga elemental depth profiles in CIGS (film A) and ACIGS (film C) films. Profiles were measured by SIMS from film front surface (left) to Mo interface (right).

Figure 11: Comparison of Ga/(In+Ga) composition profiles in CIGS (film A) and ACIGS (film C) films. Profiles were measured by SIMS from film front surface (left) to Mo interface (right). (Ag+Cu)/(In+Ga) composition profile in each film is also plotted as reference.

reading monotonically increases with the film emissivity [63]. Figure 12 shows the floating thermocouple reading in typical CIGS and ACIGS three-stage growth (containing all three stages), during the time frame near the end of the second stage. Both of the floating thermocouple readings show an inflection point near 110 min, which corresponds to the film stoichiometry point. After the stoichiometry point, the rate of increase in the floating thermocouple readings is higher in the CIGS film growth than in the ACIGS film growth. This indicates the change rate of the CIGS film emissivity is higher than the ACIGS film when they transition from stoichiometry to group-I rich composition. According to flux calculation based on deposition temperature and tooling factor, the Cu flux was 0.6×10^{-8} mol/s for the CIGS film deposition, and the Cu flux of 0.6×10^{-8} mol/s and Ag flux of 0.2×10^{-8} mol/s used for the ACIGS film. Even though the secondary phases were deposited faster in the ACIGS growth, its emissivity change was still slower. This can be attributed to the significantly smaller surface coverage by the secondary phases on the ACIGS film than on the CIGS film, as shown in the TEM composition mapping.

4. Summary and Conclusion

Group-I rich ACIGS films with three different Ag/(Ag+Cu) ratios were grown by the three-stage co-evaporation process but only until the end of the second stage. SIMS depth profiling confirmed the existence of the secondary phases on the film surfaces with the rest of the bulk remaining stoichiometric chalcopyrite ACIGS. It also showed an accumulation of Ag in the secondary phases with higher Ag/(Ag+Cu) than in the chalcopyrite phase. However, as revealed by EDS mapping in TEM, the Ag-Cu-Se secondary phases intermixed with the chalcopyrite phase on the film surfaces, while the Cu-Se secondary phases formed a separated layer covering most of the film surfaces. As Ag/(Ag+Cu) increased from 0 to 0.3 to 0.6, the secondary phases changed their crystal structure following the Cu_2Se – Ag_2Se pseudo-binary tie-line, as identified in the GIXRD of pure Ag-Cu-Se films with similar Ag/(Ag+Cu) as in the group-I rich ACIGS films. In addition, the surfaces of the group-I rich ACIGS films became smoother with reduced facets and voids as more Ag is incorporated into the secondary phases. At the point where the films transition from the chalcopyrite bulk to the surface region containing the secondary phases, Na segregation appeared and was suppressed in the films containing Ag. Because of the location and distribution of the secondary phases which were controlled by Ag/(Ag+Cu), the incorpora-

Figure 12: Floating thermocouple readings during the second stage of a three-stage growth of a CIGS and a ACIGS films. The inflection point near 110 min on each curve corresponds to the film stoichiometry point.

tion of Ag reduced the film emissivity change when the films became group-I rich. It would also reduce the slope of the Ga/(In+Ga) double gradients, if the films continued to be deposited by complete three stages.

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