

EFFECT OF REACTION TEMPERATURE ON Cu(InGa)(SeS)₂ FORMATION BY A SEQUENTIAL H₂Se/H₂S PRECURSOR REACTION PROCESS

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ABSTRACT

The effect of sulfization temperature on Ga through-film uniformity in a 2-reaction H₂Se/H₂S precursor process for Cu(InGa)(SeS)₂ was studied. Cu_{0.8}Ga_{0.2}/In bi-layer precursors were prepared by sputter deposition. The precursors were then partially selenized at 450 °C, followed by sulfization at temperatures ranging from 450 to 550 °C. The observed threshold temperature for Ga homogenization during sulfization was ~500 °C. It is speculated that this threshold temperature possibly derives from a solid→liquid phase transition at 485 °C on the Ga-rich edge of the γ 1-Cu₉Ga₄ phase region.

INTRODUCTION

The chalcogenization of Cu-In-Ga precursors has yielded Cu(InGa)(SeS)₂ absorber layers with photovoltaic conversion efficiencies in excess of 13% at both the device and module scales [1,2]. A critical issue for the 2-reaction selenization/sulfization precursor process is control of the through-film composition to prevent Ga accumulation at the back of the film. In particular, through-film Ga uniformity has not been observed at a sulfization temperature of 480 °C [2,3], while it is seen at 500 °C and above [1]. Back-contact Ga accumulation depletes Ga from the active region of the resultant device, preventing the realization of higher open-circuit voltages. A proven technique for uniformly re-distributing Ga that has accumulated at the back contact during selenization is to only *partially* selenize the Cu-In-Ga precursor before sulfization at temperatures exceeding ~500 °C [1]. The partial selenization reaction yields indium-rich Cu(InGa)Se₂ co-existing with a slow-selenizing Cu₉Ga₄ intermetallic [4]. The existence of Cu₉Ga₄ at the commencement of the sulfization step qualitatively correlates with increased through-film Ga uniformity in the resultant Cu(InGa)(SeS)₂ film. Films that are more extensively selenized exhibit a significantly reduced degree of Ga homogenization [5,6].

In spite of the success of this approach, the precise dependence of through-film Ga uniformity on sulfization temperature has not been published, nor have hypotheses into the Ga homogenization mechanism been developed. This paper seeks to address these issues.

EXPERIMENTAL

Cu_{0.8}Ga_{0.2}/In bi-layer precursors were prepared by sequentially sputtering first Cu_{0.8}Ga_{0.2} alloy then elemental In onto 1"×1" Mo/soda-lime (SL) glass substrates. Targeted thicknesses of the Cu_{0.8}Ga_{0.2} and In layers were 3490 Å and 4890 Å, respectively, to yield a final Cu(InGa)(SeS)₂ thickness of 2 μm with overall composition ratios Cu/(In+Ga) = 0.90 and Ga/(In+Ga) = 0.22. The thickness of the Mo back contact and SL substrates were 0.7 μm and 2 mm, respectively.

The 2-step chalcogenization reactions were carried out in a 2"-diameter quartz tube reactor heated by an external heating jacket. Two samples were reacted per run, and were positioned adjacently in an upstream/downstream orientation.

Chalcogenization reactions were performed using H₂Se and H₂S in sequence. The hydride gases were present at concentrations of 0.35 mol% in 1 atm flowing Ar carrier gas. O₂ was also present at a concentration of 0.0035 mol%. Samples were first selenized at a temperature of 450 °C for 15 minutes, and then sulfized for 30 minutes at temperatures ranging from 450 to 550 °C. Samples were pushed into and pulled from the heated reaction zone to respectively initiate or terminate the chalcogenization reactions. Two series of runs were conducted, and are denoted "Series 1" and "Series 2." The second series of experiments were conducted to verify the trends observed in the first series.

Films were characterized by scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), x-ray diffraction (XRD) using CuK α ₁ incident radiation, and Auger electron spectroscopy (AES) depth profiling.

RESULTS

Partially-selenized film composition

The composition of the partially-selenized film measured by EDS on the front surface was Cu/(In+Ga) = 0.93 and Ga/(In+Ga) = 0.05, consistent with earlier work [4]. The expected presence of the γ 1-Cu₉Ga₄ intermetallic phase was also verified in the present study by mechanically lifting-off the overlying chalcopyrite film to expose the Mo back contact (Figure 1).

Effect of sulfization temperature on chalcopyrite composition

Figure 2 exhibits chalcopyrite (112) line scans of selected films sulfized at temperatures ranging from 450 to 550 °C. It is assumed that changes in peak shape and position are due to variations in composition. The peak maxima slowly shift to higher 2θ values (indicating higher degrees of Ga and/or S incorporation into the bulk chalcopyrite) with increasing temperature from 450 to ~500 °C. At ~500 °C, however, there appears to be a step increase in the 2θ positions of the peak maxima, indicating an abrupt increase in Ga or S incorporation into the bulk of the chalcopyrite. Features such as the broadening of the low- 2θ 500 °C peak and the low- 2θ shoulder on the 523 °C peak are not well characterized at this point. Figure 3 summarizes the XRD data for all reacted films, and emphasizes the discontinuity in d-spacing that occurs in the vicinity of 500 °C. In fact, multiple sample pairs processed adjacently in the range 500 – 510 °C exhibit discontinuous d-spacings. Also apparent in Figure 3 is a systematically higher d-spacing in the Series 2 data.

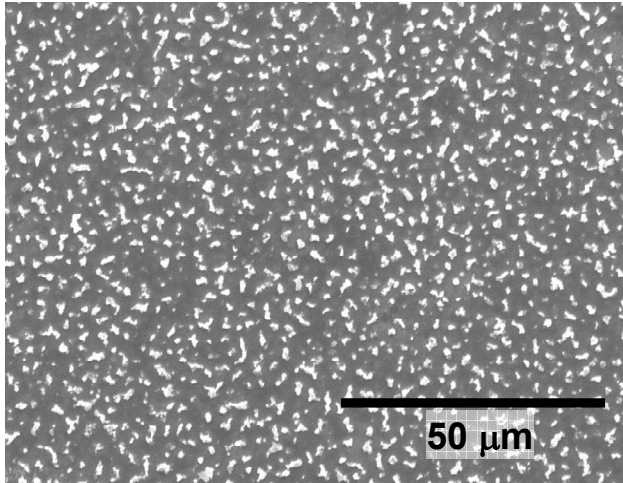


Figure 1. γ 1- Cu_9Ga_4 intermetallics (white) on Mo back contact (gray background) after reaction of precursor film in H_2Se for 15 minutes at 450 °C. The intermetallics were exposed by mechanically lifting-off the $\text{Cu}(\text{InGa})\text{Se}_2$ film formed during the selenization reaction.

As XRD d-spacings do not indicate whether a peak shift is due to Ga or S incorporation, the composition of all samples were measured by EDS, and selected samples were also characterized by AES depth profiling. EDS samples to a depth of 0.5 – 1.0 μm , and therefore provides some indication of the quantity of Ga that has been redistributed from the back contact into the bulk of the chalcopyrite during sulfization. For example, if the $\text{Ga}/(\text{In}+\text{Ga})$ ratio by EDS is ~0.2, it is assumed that the Ga profile is substantially uniform.

Figure 4 shows $\text{Ga}/(\text{In}+\text{Ga})$ atomic ratios measured by EDS over the range of sulfization temperatures. As sulfization temperature increases, the Ga content

increases, indicating the redistribution of Ga from the back contact into the bulk of the chalcopyrite film. The data indicate that a sulfization temperature of 500 °C is a necessary process parameter to approach a uniform Ga profile, but is not sufficient in all cases. The Series 2 data in Figure 4 shows a systematically lower Ga composition, indicating films with reduced Ga incorporation into the bulk of the chalcopyrite, consistent with the behavior exhibited in Figure 3.

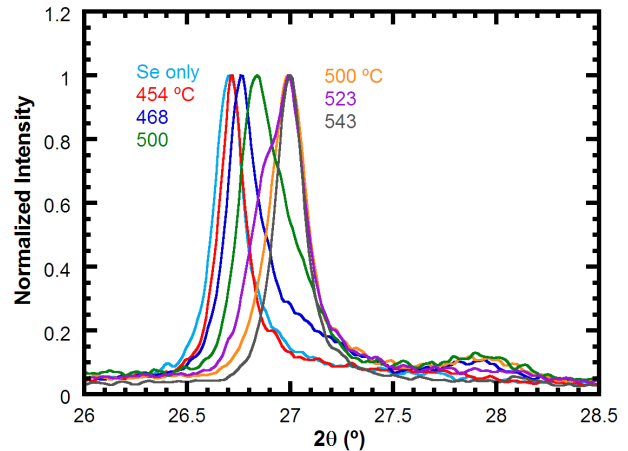


Figure 2. Selected $\text{Cu}(\text{InGa})(\text{SeS})_2$ XRD line profiles exhibiting higher degrees of Ga and/or S incorporation (higher 2θ values) with increasing sulfization temperature as indicated. “Se only” indicates a partially selenized film without subsequent sulfization. An apparent step increase in Ga and/or S incorporation is observed in the vicinity of 500 °C.

Figure 5 shows $\text{S}/(\text{Se}+\text{S})$ atomic ratios measured by EDS and indicates $\text{S}/(\text{Se}+\text{S})$ increasing by 2 to 3 times from 450 to 500 °C, followed by a possible slight decrease in the temperature range 500 – 550 °C.

Selected samples were further characterized by AES depth profiling, shown in Figure 6. Sample AES1 is an atypical sample which exhibits a low chalcopyrite lattice d-spacing, due to higher sulfur incorporation as opposed to increased Ga incorporation into the bulk chalcopyrite. Sample AES2 is a representative graded Ga sample that exhibits a d-spacing on the high side of the observed discontinuity. Sample AES3 exhibits a Ga profile that is approximately 70% uniform, though it is not completely homogeneous. This sample also exhibits the lowest degree of S incorporation in spite of being sulfized at 550 °C. The reduced S incorporation in AES3 compared to the 510 °C samples is consistent with the downward $\text{S}/(\text{Se}+\text{S})$ trend from 500 to 550 °C in Figure 5.

DISCUSSION

Broadly speaking, the data in the present study are generally consistent in suggesting an abrupt increase in Ga incorporation into the bulk chalcopyrite film near 500

°C, but improvements in the experimental reproducibility are necessary to more definitively quantify the observations. In particular, the systematically reduced Ga uniformity in the Series 2 data indicates that the process does not yet possess a sufficiently high degree of reproducibility. Nevertheless, a number of hypotheses can be drawn from the data.

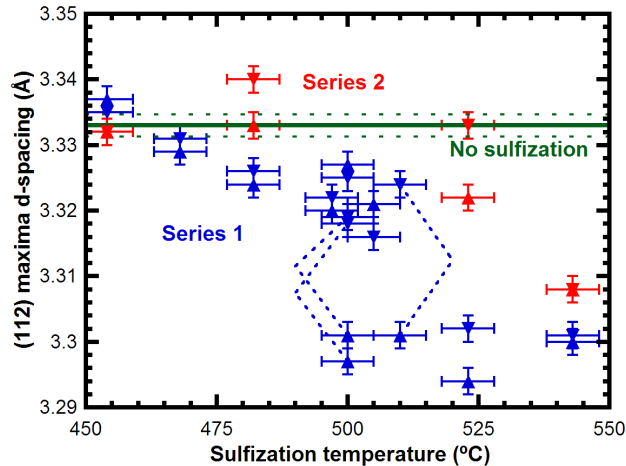


Figure 3. $\text{Cu}(\text{InGa})(\text{SeS})_2$ (112) maxima d-spacing as a function of sulfization temperature. The blue dashed connecting lines emphasize three sample pairs (both samples reacted adjacently) that exhibit wide d-spacing variation. Upstream and downstream samples are denoted by (\blacktriangle) and (\blacktriangledown), respectively. The green “No sulfization” line represents d-spacing for selenized-only samples, with the green dashed line indicating corresponding experimental uncertainty.

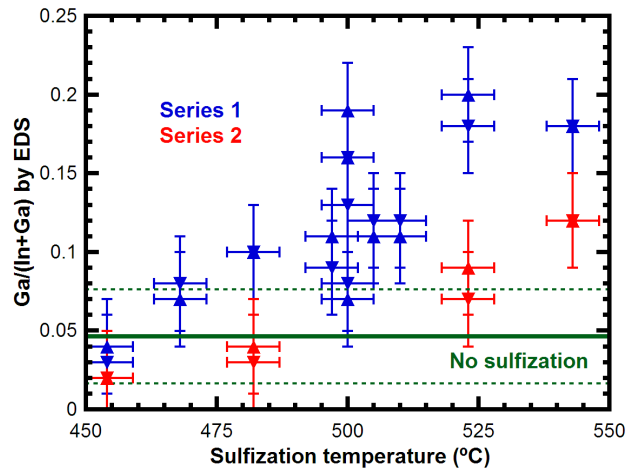


Figure 4. $\text{Ga}/(\text{In}+\text{Ga})$ atomic ratios measured by EDS.

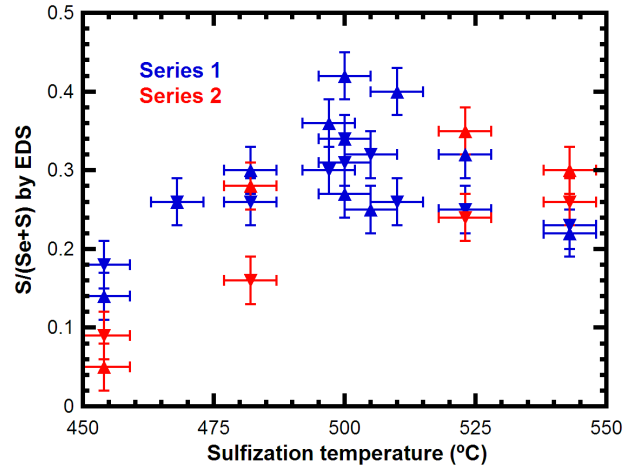


Figure 5. $\text{S}/(\text{Se}+\text{S})$ atomic ratios measured by EDS.

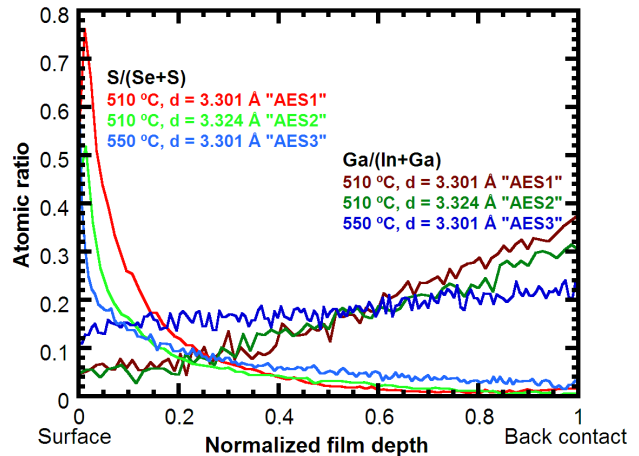


Figure 6. Through-film AES composition profiles of three samples, indicating reduced chalcopyrite (112) d-spacing due to either uniform Ga (“AES3”) or increased S (“AES1”) incorporation. Samples sulfized at 510 °C were reacted adjacently – with sample “AES1” in the upstream position. Credit: Joel Pankow, NREL.

Effect of composition on chalcopyrite d-spacing

The issue of whether Ga or S is primarily responsible for influencing d-spacing is addressed in Figures 7 and 8, which compare composition ratios by EDS to (112) d-spacings. With few exceptions, $\text{Ga}/(\text{In}+\text{Ga})$ and d-spacing correlate linearly as would be expected by a Vegard’s law approximation. By contrast, a similar correlation is not observed between $\text{S}/(\text{Se}+\text{S})$ and d-spacing. Taken together, Figures 7 and 8 indicate that in most cases, it is Ga incorporation into the bulk chalcopyrite that is responsible for d-spacing reduction. Therefore it is inferred that the observed discontinuity in d-spacing at 500 °C is due to an abrupt change in Ga mobility. Samples AES1-AES3 are noted in the figures, emphasizing the atypical combination of high S incorporation, low Ga uniformity, and low d-spacing in sample AES1.

It should be noted that caution must be taken when drawing conclusions based on d-spacing maxima, particularly given the high degree of structure in the line profiles in Figure 2, and the composition gradients indicated by the AES depth profiles in Figure 6. However, when viewed in conjunction with the EDS data of Figure 4, a reasonable indication of the bulk chalcopyrite composition can be inferred.

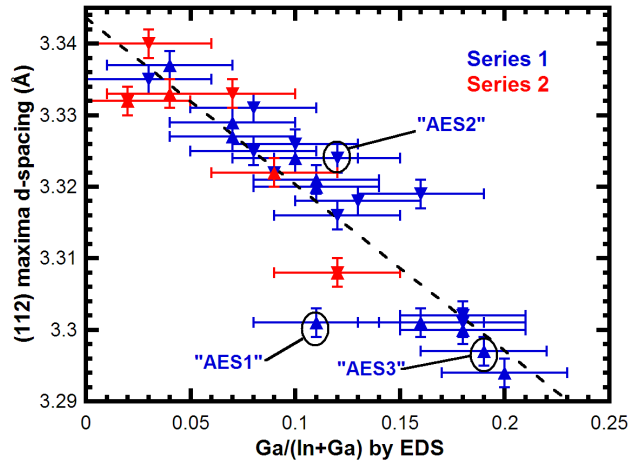


Figure 7. Correlation of (112) d-spacing to Ga/(In+Ga) measured by EDS, with the least-squares fit trend line. Samples AES1, AES2, and AES3 are compositionally profiled in Figure 6. A linear functionality is consistent with a Vegard's law approximation relating Ga/(In+Ga) to d-spacing.

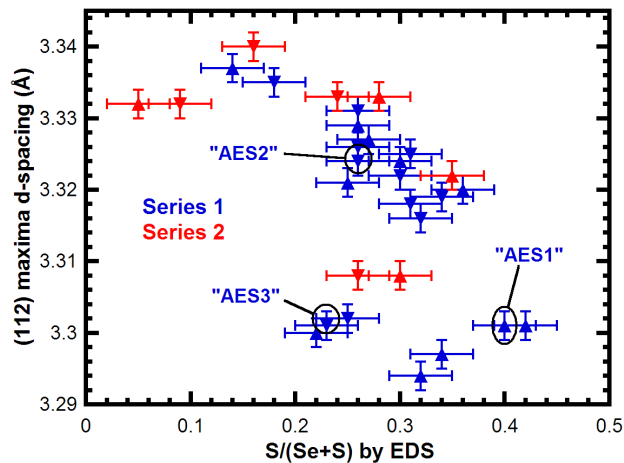


Figure 8. Correlation of (112) d-spacing to sulfur uptake. Low d-spacings are observed for a 2× range of S/(Se+S) atomic ratios, indicating that d-spacing is not primarily influenced by S/(Se+S) ratio.

Hypothesis relating to Ga mobility

The abrupt change in Ga grading at sulfization temperatures near 500 °C is further emphasized by the result that samples processed adjacently in the same

selenization/sulfization experimental run can exhibit discontinuities in d-spacing. This suggests a very high sensitivity to temperature near 500 °C. The observation of this abrupt transition in the XRD data, and also in the EDS data, suggests that the Ga homogenization mechanism is not simple solid-state diffusion, which would not yield a step increase with temperature.

It has been repeatedly shown that “excessive” selenization suppresses Ga mobility during sulfization [1,6]. It has also been shown that In (either elemental or alloyed) selenizes more rapidly than Ga [4,7]. To a first approximation, the reaction can be considered to occur sequentially, with In selenizing before Ga to form In-rich $\text{Cu}(\text{InGa})\text{Se}_2$ and $\gamma\text{-Cu}_9\text{Ga}_4$. If the selenization reaction is carried “excessively” far, the Cu_9Ga_4 begins to selenize, albeit slowly, and is incorporated as Ga-rich $\text{Cu}(\text{InGa})\text{Se}_2$ near the back contact. While a rigorous causation has not been demonstrated, a reduced quantity of Cu-Ga intermetallic qualitatively correlates to reduced Ga mobility during sulfization. Considering the abrupt change in Ga mobility and the expected presence of $\gamma\text{-Cu}_9\text{Ga}_4$, a hypothesis relating to Ga mobility can be drawn from the solid-liquid equilibria of the Cu-Ga phase diagram [8]. At temperatures below 485 °C, the Ga-rich edge of the $\gamma\text{-Cu}_9\text{Ga}_4$ region is bordered by other solid Cu-Ga intermetallic phases. Above 485 °C, however, $\gamma\text{-Cu}_9\text{Ga}_4$ can exist in equilibrium with a liquid Ga(Cu) phase. It is hypothesized that the existence of a liquid Ga phase may provide the requisite mobility for Ga homogenization.

If metallic Ga possesses the requisite mobility for incorporation into the bulk chalcopyrite, a re-examination of the present method of sulfization is necessary. Ga sulfization may be in competition with the homogenization process. Elemental or metallic Ga at >500°C may be enabling Ga mobility while sulfization may simultaneously be immobilizing Ga by binding it into the chalcopyrite lattice. The ability of temperature alone to homogenize Ga has already been demonstrated by the use of argon annealing at >500 °C to yield homogeneous $\text{Cu}(\text{InGa})\text{Se}_2$ from selenized Cu-In-Ga precursors [9,10]. The repeated observation in the present study of samples processed side-by-side that exhibit significantly different degrees of Ga homogenization suggests that the reactor is currently operating in a regime that is highly sensitive to either temperature or S concentration variations. The current sulfization method of heating the sample in an S-containing atmosphere may be an inherently non-robust process in terms of the resultant Ga profile.

Future work

An obvious shortcoming of the data is the reduced degree of Ga homogenization observed in Series 2. While this behavior is suggestive of the reduced Ga mobility resulting from “excessive” selenization, it could be due to any number of factors given the number of process variables. Changes in heater jacket temperature calibration, sputter thickness, or hydride gas flow

calibration, could all contribute to the observed experimental irreproducibility.

It is suggested that two modifications be made to the experimental protocol to improve reproducibility. First, lowering the selenization temperature will slow the reaction and should improve the time resolution of the selenization process. Currently, a significant percentage of the 15 minute reaction time occurs during the 3-5 minutes required for the samples to heat up to the selenization temperature after being pushed into the reaction zone [11]. If excessive selenization is the cause for the poor Ga uniformity in the Series 2 data, improving the time resolution is expected to reduce the probability of excessive selenization, thereby improving the reproducibility of the Ga homogenization. Second, an investigation should be conducted into an inert anneal above 500 °C preceding the introduction of H₂S into the reactor. By decoupling the effects of temperature and sulfur, it should be possible to demonstrate whether temperature or sulfur is driving Ga homogenization. This approach may also ultimately yield a more robust baseline process. Alternately, to gain greater insight into the Ga homogenization mechanism, higher H₂S concentrations should be investigated to observe if Ga homogenization is inhibited. Reduced Ga mobility with increasing sulfur concentrations would support the hypothesis of Ga mobility being derived from its existence in an elemental or metallic phase.

A second shortcoming in the experimental results is the low d-spacings observed for films that were either not sulfized or sulfized below 485 °C. Pure component CuInSe₂ exhibits a d-spacing of 3.351 Å, higher than any of the observed d-spacings. For example, the d-spacing of the unsulfized films correlates to a Ga(In+Ga) ratio of ~0.12, inconsistent with corresponding EDS measurements. It is speculated that there may be residual stress in the films following the chalcogenization reactions.

CONCLUSIONS

It was found that a sulfization temperature in excess of 500 °C is necessary to achieve Ga homogenization in 2-reaction selenization/sulfization processes. There also appears to be an abrupt increase in Ga mobility, leading to increased Ga uniformity, which occurs near 500 °C. It is hypothesized that this abrupt increase may be due to a solid→liquid phase transition that occurs on the Ga-rich edge of the γ 1-Cu₉Ga₄ phase region. Refinements to the experimental protocol, such as lower selenization temperature and the introduction of an inert anneal above 500 °C prior to sulfization, are suggested to improve the experimental reproducibility and provide quantitative improvements for further characterizing the Ga homogenization mechanism.

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