Alkali Dispersion in (Ag,Cu)(In,Ga)Se$_2$ Thin Film Solar Cells—Insight from Theory and Experiment

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ABSTRACT: Silver alloying of Cu(In,Ga)Se$_2$ absorbers for thin film photovoltaics offers improvements in open-circuit voltage, especially when combined with optimal alkali-treatments and certain Ga concentrations. The relationship between alkali distribution in the absorber and Ag alloying is investigated here, combining experimental and theoretical studies. Atom probe tomography analysis is implemented to quantify the local composition in grain interiors and at grain boundaries. The Na concentration in the bulk increases up to $\sim$60 ppm for $[\text{Ag}]/([\text{Ag}] + [\text{Cu}]) = 0.2$ compared to $\sim$20 ppm for films without Ag and up to $\sim$200 ppm for $[\text{Ag}]/([\text{Ag}] + [\text{Cu}]) = 1.0$. First-principles calculations were employed to evaluate the formation energies of alkali-on-group-I defects (where group-I refers to Ag and Cu) in (Ag,Cu)(In,Ga)Se$_2$ as a function of the Ag and Ga contents. The computational results demonstrate strong agreement with the nanoscale analysis results, revealing a clear trend of increased alkali bulk solubility with the Ag concentration. The present study, therefore, provides a more nuanced understanding of the role of Ag in the enhanced performance of the respective photovoltaic devices.

KEYWORDS: ACIGS, CIGS, solubility limit, atom probe, density functional theory, first-principles calculations

1. INTRODUCTION

Cu(In,Ga)Se$_2$ (CIGSe) photovoltaics is a promising technology combining high power conversion efficiency (PCE), relatively low production cost, excellent outdoor stability, and high radiation hardness. One effective way of enhancing the device performance is by tuning the bandgap energy ($E_g$) at different parts of the absorber via adjusting the absorber composition profiles, which in effect also improves band alignment and suppresses recombination at interfaces. CIGSe is thermodynamically stable within a wide range of chemical compositions at usual deposition temperatures, allowing bandgap engineering by alloying, which motivates the efforts to further boost the PCEs. Tailoring of $E_g$ by alloying can be achieved during processing through varying the composition of the quaternary alloy, typically the $[\text{Ga}]/([\text{Ga}] + [\text{In}])$ ratio (referred to as GGI), incorporation of an additional alloying element (such as Al, Ag, S, or Te), or combinations thereof. For CIGSe, the band gap varies from $\sim$1.0 eV for CuInSe$_2$ to $\sim$1.7 eV for CuGaSe$_2$, making the alloy suitable not only for single-junction solar cells but also for tandem applications.

Alloying with Ag to form (Ag,Cu)(In,Ga)Se$_2$ (ACIGSe) allows lowering the deposition temperature because of a reduction of the melting point, an improvement of the crystal quality, an increase in the carrier collection length, and an enhancement of the open-circuit voltage ($V_{OC}$). Ag substitutes Cu in the lattice structure, which decreases the p$-$d hybridization, inducing a downward shift of both band edges and a slight band gap widening. It has been established that an $[\text{Ag}]/([\text{Ag}] + [\text{Cu}])$ value (referred to as AAC) of approximately 0.2 (at a GGI value of $\sim$0.45) is optimal for improving the PCE of single-junction solar cells. Hence, ACIGSe is a highly interesting chalcogenide alloy that may eventually outcompete...
CIGSe if the merits of the Ag addition for PCE offset the higher cost of raw materials.

Addition of alkali elements into the CIGSe absorber bulk or at its surface is another common practice because of the positive effect on device performance. Increased \( V_{OC} \) and fill factor (FF) are frequently reported for alkali-treated devices, stemming from the increased hole carrier density (improved conductivity) and presumably grain boundary (GB) passivation optimizing local band bending. Alkali elements have limited solubility in CIGSe grain interiors (GIs), with preferential segregation to lattice defects and phase boundaries in the polycrystalline film. This is especially apparent for heavy alkali elements (referring to K, Rb, or Cs) because of the higher defect formation energies and increased diffusion barriers in bulk CIGSe. Nonetheless, because the volume fraction of GBs is small compared with that of the GIs, the integral Na amounts can be comparable. An ambiguity with bulk incorporation, however, is that the most stable alkali-on-Cu defects (Alk\(\text{Cu} \)) are charge neutral, and thus electrically inactive. In an attempt to reconcile these results with the observed changes in the hole concentration, a kinetic model of alkali out-diffusion from GIs to GBs upon cooling was developed. The situation became even more complicated when a combination of Na with heavy alkali treatments demonstrated even higher PCEs in CIGSe compared to single-alkali postdeposition treatment (PDT). Studies on the diffusion mechanism of alkali elements in CIGSe have shown that an interplay occurs between light (referring to Li and Na) and heavy alkalis regarding their distribution in the GIs and at GBs, which is influenced by the substrate temperature as well as the alkali supply dose. There is still an ongoing debate whether the positive effects of alkali incorporation are related to their dispersion in the GIs or GBs, as well as their modification of the absorber surface. Furthermore, it is reasonable to suppose that the incorporation and influences of alkali elements could vary when the CIGSe absorber is modified by Ag alloying, as described above.

Alkali elements can be introduced via predeposition treatment (alkali-containing precursor layer), coevaporation, or PDT, where the light and/or heavy alkali elements can be chosen. For heavy alkali elements, PDT is the most common supply technique, whereas light alkali elements can be supplied with all three techniques. Substantial incorporation of alkali elements is also caused by in-diffusion from glass substrates during processing if no diffusion barrier is used. Irrespective of the selected alkali element or doping technique, it has been shown that there is an optimum alkali amount, which if exceeded leads to degradation of \( V_{OC} \) and lower PCE values, observed in both CIGSe and ACIGSe. The effect seems to be more severe in the case of ACIGSe, where the PCE can drop significantly. It has also been reported for Ag-alloyed CuInSe\(_2\) (ACISe). This could be anticipated because the optimum amount of KF PDT for ACIGSe was found to be lower compared to CIGSe synthesized under similar conditions. Understanding the underlying cause of this distinction is critical to further development of successful PDT strategies. Although the reason for this variance is currently unknown, it could be because of the differences in solubility limits for alkalis (i.e., a thermodynamic effect) or rate of in-diffusion from the alkali-rich source (i.e., a kinetic effect). There are some studies supporting both hypotheses. Kim et al. showed using secondary ion mass spectrometry (SIMS) that the Na concentration in the absorber increases upon addition of Ag in CIGSe grown on soda-lime glass (SLG) substrates, with the authors arguing in favor of faster in-diffusion of alkalis in ACIGSe. However, in a more recent study of ACIGSe/CIGSe tandem devices, the same authors presented SIMS profiles with nearly an order of magnitude stronger Na signal within the ACIGSe top layer compared to the CIGSe bottom cell. Considering that the only source of alkalis was the SLG substrate, all Na in the top cells must have diffused through the bottom CIGSe cell first. As such, the preference for Na accumulation in the top ACIGSe cell points to higher alkali solubility in ACIGSe.

It, therefore, remains unclear how alkali elements are distributed in ACIGSe and what role they play in enhancing the performance of CIGSe devices upon Ag alloying. Among the few experimental techniques capable of investigating local compositions of GBS and GIs, atom probe tomography (APT) has proven exceptionally useful for quantitative elemental mapping in three dimensions. To utilize this unique capability, we perform in this work a comparative APT characterization of alkali distributions in polycrystalline ACIGSe and CIGSe films. Additionally, we employ first-principles calculations within the density functional theory (DFT) to verify and explain the experimental trends in solubility. With the synergy of these methods, we can draw a clearer picture of the complex phenomena behind the improved efficiency of ACIGSe and CIGSe absorbers with alkali incorporation.

### 2. EXPERIMENTAL AND COMPUTATIONAL METHODS

#### 2.1. Solar Cell Processing

Two different glass substrates were used, namely SLG, which is Na-rich and high-strain glass (HSG), which is K-rich. Mo back contacts were DC-sputtered (target purity 99.97%) on the cleaned glass substrates, followed by evaporation of \( \sim 15 \) nm thick NaF alkali precursor layers. CIGSe, ACIGSe, and Ag(In,Ga)\(_2\)Se\(_3\) (AIGSe) absorbers were coevaporated in a three-stage...
process using metal targets (99.999% purity) and 4N Se target (99.99% purity). The three-stage process follows an evolution profile consisting of I-poor, I-rich, and finally I-poor stages, with all stages having the same \([\text{Ag}] / [\text{Cu}]\) ratio for ACIGSe. The CIGSe (Ag-free, AAC = 0) and AIGSe (Cu-free, AAC = 1) devices grown on SLG were produced here to be used for comparison (reference samples). The substrate temperature was about 400 °C in the first stage and ramped up to about 550 °C in the following two stages. The deposition time for the absorber layers was about 30 min, resulting in film thicknesses of around 2 μm. High-Ga and low-In deposition rates were used at the initial stage of the absorber deposition to induce a Ga grading at the back contact. The elemental AAC, GGI, and \([(\text{Ag} + [\text{Cu}] / [\text{Ga} + [\text{In}]] / (\text{I}/[\text{III}])\) ratios in the absorbers were determined using X-ray fluorescence (XRF) spectroscopy. KF PDT was performed on all samples for 10 min after ramping down the substrate temperature to 350 °C at a rate of approximately 5 °C/min. A 40 nm CdS buffer layer was deposited using chemical bath deposition (CBD). A 125 ml solution with 4.5 mM Cd acetate and 1.7 M ammonium hydroxide was preheated in a 60 °C water bath, after which 50 ml of thiourea (0.35 M) was added and the samples were immersed. The CdS growth was terminated after 6 min, after which the samples were rinsed and dried. Schematic of the four samples investigated is shown in Figure 1. Devices used for electronic measurements were completed by depositing a front stack of 100 nm of undoped ZnO, followed by 200 nm of ZnO/Al using RF magnetron sputtering (both targets of 99.99% purity). A metal stack of Ni—Al—Ni was deposited by electron beam evaporation through a shadow mask (target purity: 99.9% Ni and 99.999% Al). Finally, cells with an area of 0.5 cm² were fabricated to 25 °C controlled to 25 °C.

3. RESULTS AND DISCUSSION

3.1. Absorber Composition and Device Performance.

The absorber compositions were initially determined by XRF. The elemental AAC, GGI, and [I]/[III] of each sample are presented in Table 1. Device characteristics of the respective samples are presented in Table 2. For ACIGSe, the absorber deposited on HSG showed slightly higher \(J_{SC}\) and PCE values compared to the films grown on SLG.

3.2. Alkali Distribution Profiles along the ACIGSe Absorber Thickness.

Figure 2 shows GDOES profiles of alkalis in ACIGSe absorbers grown on the different substrates. The profiles start at the CdS/ACIGSe interface and end in the Mo layer. The absorber film grown on HSG was slightly thinner compared to the one grown on SLG, with the measured thicknesses of ~1.7 and ~2.1 μm, respectively (determined by XRF and verified with cross-sectional SEM images). Both films displayed an increase in Na and K concentrations at the CdS/ACIGSe and ACIGSe/Mo interfaces. As expected, the K increase at the back contact is more pronounced for the HSG substrate. Similar alkali profiles were reported in our previous work for CIGSe and ACIGSe, as well as in multiple other studies reviewed in ref 22.

The main optoelectronic effects of alkali segregation at the interfaces are suggested to be similar to those of alkalis dispersed in GBs, such as defect passivation and local band bending. However, in addition, alkali enrichment at the heterojunction can promote alkali-rich compound formation (such as AlKInSe₂), interactions with ordered defect compound (ODC) phases, as well as altering the growth behavior of the buffer layer. Surface chemical analysis was performed here using energy-dispersive X-ray spectroscopy (EDS) in SEM and revealed no alkali-rich compounds, despite the clear alkali enrichment identified at the absorber surface using GDOES. Thus, the quantities of these compounds were below the sensitivity limit of EDS or they were not stable under the electron beam. In our previous study on alkali treatment of ACIGSe, we demonstrated that the alkali-rich surface compound, \((\text{Ag,K})\text{InSe}_2\), only begins to form in samples treated with an excessive dose of KF. It is necessary to mention, however, that GDOES provides only qualitative analysis of the alkali distribution. Furthermore, it delivers in-depth compositional information averaged over a spot with a diameter of ~2 mm. Hence, interpretation of the GDOES

Table 1. Integral Absorber Compositions Measured with XRF

| Sample   | AAC | GGI | \([\text{I}]/[\text{III}]\) |
|----------|-----|-----|-------------------------|
| CIGSe-SLG | 0   | 0.38| 0.89                    |
| AICIGSe-SLG | 0.22 | 0.40 | 0.89                 |
| AICIGSe-HSG | 0.19 | 0.43 | 0.87                 |
| AIGS-SLG  | 1   | 0.40| 0.85                    |

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scans should be made with caution. Local compositional analysis was performed here on the CdS/ACIGSe interface using APT, where alkali segregation was found to be inhomogeneous at the nanometer scale (see Figure S1 in Supporting Information), that is, partial segregation occurs across the entire interface. This indicates that at a fine scale, the alkali is most likely to be distributed as islands at the CdS/ACIGSe interface. The alkali concentrations at the interface are well below 1 at. %, which is unfortunately not possible to map using SEM-EDS, for instance.

It seems likely that the alkali segregation detected using GDOES near the surface is not connected with nucleation of ODGs because no clear group-I depletion is observed (not presented here). The formation of ODGs is governed by the

| sample            | $V_{OC}$ [mV] | $J_{SC}$ [mA/cm²] | FF [%]     | PCE [%]     |
|-------------------|---------------|-------------------|------------|-------------|
| CIGSe-SLG         | 704 (706 ± 3) | 31.8 (30.7 ± 0.3) | 75.3 (75.0 ± 1.2) | 16.8 (16.3 ± 0.4) |
| ACIGSe-SLG        | 769 (761 ± 6) | 30.2 (30.1 ± 0.2) | 77.9 (74.8 ± 2.6) | 18.1 (17.4 ± 0.7) |
| ACIGSe-HSG        | 770 (759 ± 10)| 31.0 (30.7 ± 0.2) | 77.7 (76.8 ± 0.6) | 18.6 (17.9 ± 0.5) |
| AIGSe-SLG         | 682 (667 ± 5) | 25.1 (24.4 ± 0.9) | 68.2 (66.4 ± 1.7) | 11.6 (10.7 ± 0.4) |

$^a$Average values with their standard deviations are given in parentheses.

Figure 2. GDOES depth profiles for ACIGSe samples on (a) SLG and (b) HSG, showing K and Na signals from the CdS/ACIGSe interface to the Mo back contact. The onset of the Mo signal is marked in red color.

Figure 3. APT analysis of GBs in the CIGSe (SLG) and both ACIGSe samples. 1D concentration profiles are shown below the respective reconstructions. The uppermost reconstructions show overlaid Se (blue), K (black), and Na (green) atoms, with individual reconstructions for alkalis shown separately below. (a) CIGSe grown on SLG (reference) showing four GBs in the absorber and a Na-decorated dislocation. Some GBs appear thicker because the GB planes are not parallel to the viewing direction. The 1D profile is measured across the GB highlighted by dotted arrows. (b) ACIGSe grown on SLG and (c) ACIGSe grown on HSG, both showing one GB per reconstruction.
3.3. Nanostructure Analysis of Alkali Dispersion by Atom Probe Tomography. In addition to GDOES depth profiling, spatial distributions of the matrix and alkali elements in three dimensions were examined at the nanoscale using APT. The primary objective is analyzes the composition at GBs and in GIs, separately. Because of the limited volume analyzed using this technique and the compositional variations between grains, a minimum of five successful APT measurements was carried out from each sample with datasets of at least 10 million atoms, in order to attain reasonable statistics.

3.3.1. Grain Boundaries. The effect of Ag alloying on the GB composition and alkali dispersion is investigated here by analyzing the two ACIGSe samples and comparing them to the CIGSe absorber grown on SLG (Ag-free reference sample). Figure 3 shows APT analyses of the three samples. Each presented 3D reconstruction includes at least one GB. In all cases, the concentrations of matrix elements in the GBs differ from those in the adjacent grains, which is a common observation in CIGSe. The GBs here display slight Cu-depletion and In-enrichment, which is especially evident for the ACIGSe samples. Interestingly, the measured Ag profiles are almost flat, translating into an increasing AAC ratio in the GBs. According to two earlier extensive APT studies, it is now understood that the majority of GBs in CIGSe exhibit this kind of Cu-depletion. This tendency has also been reported using high-resolution XRF for CIGSe after RbF PDT. The compositional fluctuations of matrix elements at GBs are claimed to influence the electrical characteristics of solar cells because of the local band bending, which can have beneficial, detrimental, or neutral impact on the device performance. For instance, Cu-depleted GBs are argued to reduce carrier recombination because they act as hole barriers because of a downshift of the valence band maximum. Although structural information on planar defects is usually not accessible by APT, the observed features resemble random high-angle GBs and not stacking faults or twin boundaries. Such a distinction can be made from an irregular curvature of interfaces, which stems from an arbitrary connectivity of faceted grains in the absorber.

Segregation of alkali elements at the GBs is observed for all samples. Both Na and K are found in dissimilar quantities at different GBs, which agrees with previous studies on CIGSe. The effective thickness of the GBs, measured by the compositional change at the interfaces, was in the range of 4–6 nm (see Figure 3). The extent of alkali segregation can be additionally quantified by calculating the Gibbs interfacial excess (Γ) values. The values were extracted for all GBs shown in Figure 3. In the CIGSe sample, the Γ_{Na} and Γ_{K} values varied among the four GBs recognized in Figure 3a from 0.03 to 2.74 at./nm² and from 0.97 to 3.14 at./nm², respectively. In the ACIGSe sample grown on SLG, the Γ_{Na} and Γ_{K} values in the single GB seen in Figure 3b were 0.83 and 1.87 at./nm², respectively. For comparison, in the ACIGSe sample grown on HSG, the Γ_{Na} and Γ_{K} values in the GB shown in Figure 3c were 0.04 and 3.66 at./nm², respectively. Traces of O were detected at some GBs for each of the samples investigated, which is a common finding in CIGSe and CZTS absorbers. Oxygen contamination is argued to arise primarily through diffusion from the substrate and/or surface oxidation before deposition of a buffer layer. Preferential O segregation is reported for GBs with a specific misorientation angle, but no such correlation has been established for alkali elements. Herein, we observe no significant difference in the behavior of alkalis at GBs of ACIGSe and CIGSe. However, three important observations can be made: (1) concentrations of alkalis are dissimilar in different GBs within the same sample,
which is in agreement with earlier APT studies on CIGSe.\textsuperscript{40,42,61} (2) K segregation is more consistently observed compared to Na, with some GBs being nearly devoid of Na, even in the absorber grown on SLG, as seen in Figure 3a. (3) GBs in the ACIGSe sample grown on the HSG substrate show greater K segregation and only small traces of Na. Hence, this indicates that the HSG substrate is clearly the leading source of K in the GBs. According to the model/hypothesis of interplay between light and heavy alkali elements in GBs and GIs of chalcopyrite thin films (ion exchange mechanism),\textsuperscript{22,68} it is understood that heavier alkalis replace Na at the GBs if supplied in a higher dosage or if the films are deposited at higher temperatures. This mechanism is expected to be driven by thermodynamic as well as kinetic factors. An increased higher temperatures. This mechanism is expected to be driven by thermodynamic as well as kinetic factors. An increased

3.3.2. Grain Interiors. Figure 4 shows a plot for the alkali concentrations measured with APT in eight different grains of the CIGSe and ACIGSe samples, and in five different grains of the AIGSe sample. Na is found to be widely distributed in the GIs, contrary to K, which is more localized at the GBs, especially when a higher dosage of K is introduced by using HSG, as shown above. These results are consistent with the ion exchange mechanism for alkali elements.\textsuperscript{22,68} The concentration of Na in the CIGSe reference sample varies from 10 to 20 ppm in the GIs, where the detection limit here in the measurements is \( \sim 5 \) ppm. The Na concentrations in the GIs for CIGSe fit well into the range of values reported from APT measurements in the literature for CIGSe and CuInSe\(_2\) (CISE) absorbers.\textsuperscript{24,30–38} Such a consistency implies that Na reaches a solubility limit in the CIGSe bulk. Exceptional cases can be found in the literature, such as 148 ppm of Na in the GIs of CIGSe reported by Choi et al.\textsuperscript{35} using APT. In that case, a fine-structured CIGSe absorber (high defect density) with Na-containing defect clusters in the GIs was examined, which likely contributed to such a high level of Na. It is important to also point out that high alkali content values are sometimes reported for CIGSe using SIMS analysis.\textsuperscript{21,65} This quantification, however, should be treated with caution because SIMS cannot resolve alkali-enriched dislocations, stacking faults, and clustering, even if GBs and GIs are dually separated. These limitations render APT concentrations of alkalis more reliable when resolution of different areas in a microstructure is concerned. It is important to note that significantly fewer decorated defects (such as dislocations) were detected using APT in the GIs of ACIGSe samples compared to the CIGSe sample. The specimen volume analyzed with APT is limited to the three samples grown on SLG with different AAC ratios.\textsuperscript{71} The maximum concentration of Na detected in samples grown on SLG is plotted in Figure 5 to highlight the trend. As discussed in Section 1, the increase in the alkali content is more likely to be of a thermodynamic origin (higher solubility), which is investigated using first-principles calculations in the next section.

3.4. Density Functional Theory Calculations. In order to compare the solubilities of alkali elements in ACIGSe and CIGSe, we utilized DFT for computing formation energies of alkali elements on Cu or Ag site defects (Alk\(_{Cu}\) and Alk\(_{Ag}\)) as a function of the alloy composition (i.e., GGI and AAC). We only considered the substitutional defects because Alk\(_{Cu}\) is the most stable alkali-related defect in CIGSe\textsuperscript{20} and is most likely to remain dominant with addition of Ag. The defect formation energies were computed according to the following equation

\[
H^\text{form}(\text{Alk}) = E_{\text{tot}}(\text{Alk}) - E_{\text{tot}}(\text{bulk}) + E_{\text{tot}}(\text{el})
- E_{\text{tot}}(\text{Alk}^2) + \Delta \mu_1 - \Delta \mu_{\text{Alk}}
\]

where \( E_{\text{tot}}(\text{Alk}) \) and \( E_{\text{tot}}(\text{bulk}) \) are the total energies of ACIGSe with Alk\(_{Cu}\) and of the pristine supercell, \( E_{\text{tot}}(\text{el}) \) and \( E_{\text{tot}}(\text{Alk}^2) \) are the total energies (per atom) of group-I and Alk elemental ground states; \( \Delta \mu_1 \) and \( \Delta \mu_{\text{Alk}} \) are the chemical
potentials of group-I and Alk species with respect to those in the elemental ground states, respectively. The dependence on the Fermi level and all corrections in eq 1 are omitted because of the charge-neutral nature of AlkCu.

To reproduce the stochastic nature of ACIGSe while avoiding large deviations in energies because of the multiplicity of possible cationic arrangements, the total energies of the supercells computed with DFT were processed with the cluster expansion (CE) formalism using the correlation functions of truly random systems. The CE for an alkali-free alloy was constructed from energies of 100 supercells generated using the SQS algorithm, with compositions spanning the 0 \leq GGI \leq 1 and 0 \leq AAC \leq 1 range and a uniform 10 \times 10 grid. In a similar manner, CEs for supercells containing defects were constructed for each alkali separately by replacing one randomly selected group-I cation (either Cu or Ag, whenever applicable) in the alloy supercell (yielding 180 nonequivalent systems). The results obtained without CE processing are given in Supporting Information (see Figure S2) for comparison.

To estimate the chemical potentials of elements in ACIGSe, we utilize the following relation

$$\mu_{\text{ACIGSe}} = \mu_{\text{Ga}} + \mu_{\text{In}} + \mu_{\text{Se}}$$

where $x \equiv \text{GGI}$ and $y \equiv \text{AAC}$ in the equations. Obviously, in contrast with the conventional methodology for defect calculations, all chemical potentials and ACIGSe formation energy ($\Delta H_f(\text{ACIGSe})$) are functions of $(x, y)$ composition. Therefore, nontrivial thermodynamic considerations should be introduced. Herein, we extract an analytical expression for $\Delta H_f(\text{ACIGSe})$ from our earlier study by setting $T = 0 \text{ K}$ in the equation for free energy derived within the regular solution approximation. This knowledge allows relating chemical potentials as

$$\frac{\partial \Delta H_f(\text{ACIGSe})}{\partial x} = \Delta \mu_{\text{Ga}} - \Delta \mu_{\text{In}}$$

$$\frac{\partial \Delta H_f(\text{ACIGSe})}{\partial y} = \Delta \mu_{\text{Ag}} - \Delta \mu_{\text{Cu}}$$

Combining eqs 2 and 3, one can obtain a system of three equations with five unknowns. The other two free variables can be estimated from the stability diagrams according to the well-established formalism for point defect calculations. Herein, we present the results obtained for equilibrium between the ACIGSe and AlkInSe$_2$ phases. An alternative scenario of equilibrium between ACIGSe and ODC was also explored and discussed in the Supporting Information. Both approximations provide qualitatively similar results, with only one exception specified below.

The choice of equilibrium with AlkInSe$_2$ phases is stipulated by the established experimental knowledge. Specifically, formation of AlkInSe$_2$ crystals at CIGSe surfaces after alkali treatments was reported for all four considered alkali elements (Alk = Na, K, Rb, and Cs). Such crystals are assumed to be nearly Cu-free because AlkInSe$_2$ exhibits limited miscibility with CuInSe$_2$, even though Muzzillo et al. claimed successful synthesis of (Cu,K)InSe$_2$ alloys. These factors constitute AlkInSe$_2$ as a good system for extracting chemical potentials for Ga-poor CIGSe. In ACIGSe, the appearance of (Ag,K)InSe$_2$ has been detected after KF PDT in our recent work, suggesting that a similar approximation can be applied to Ag-alloyed CIGSe. With this in mind, an expression for the formation energy of AlkInSe$_2$ can be written as

$$\Delta H_f(\text{AlkInSe}_2) = \Delta \mu_{\text{Ak}} + \Delta \mu_{\text{In}} + 2\Delta \mu_{\text{Se}}$$

which can then be combined with eqs 2 and 3 to yield
The formation energies increase slightly (but consistently) with GGI. This dependence is weaker compared to that on AAC and thus should be treated with more caution. This trend might even be invisible against random variations under the growth conditions, and hence, we did not attempt to verify it experimentally. The sensitivity of this result is evident, for instance, as the formation energy of NaAg increases slightly with GGI when Ag(Ga,In)Se₂ is in equilibrium with AlkInSe₂ but decreases when an alternative approach assuming equilibrium with ODC is considered (see Supporting Information). Such a behavior is not surprising because the equilibrium with AlkInSe₂ compounds is, strictly speaking, inapplicable to Ga-rich systems because other Alk containing Ga-rich phases would segregate in those systems instead.

Despite this limitation, the computed dependences on AAC are not strongly affected by the assumed equilibrium, suggesting that both approximations are able to reasonably reproduce the actual chemistry of the alloy.

The computed energies can be used to estimate the ratio of equilibrium Na₄ concentrations in ACIGSe and CIGSe as

\[
\frac{C_{ACIGSe}(Na_4)}{C_{CIGSe}(Na_4)} = \exp \left( \frac{H_{form}^{ACIGSe}(Na_4) - H_{form}^{ACIGSe}(Na_4)}{k_B T} \right)
\]

Assuming equilibration during PDT at 350 °C, the estimated Na concentrations in ACIGSe with GGI = 0.3 and AAC of 0.2, 0.5, and 1.0 are roughly 4, 17, and 120 times higher than in CIGSe, respectively. Importantly, the predicted four-fold increase in the Na content for AAC = 0.2 is not far from our chemical quantifications of GIs using APT. The value for AAC = 0.5 is also in reasonable agreement with one order-of-magnitude higher Na content measured with SIMS in the top ACIGSe cell of the tandem device fabricated by Kim et al., but is lower than that reported in their earlier work, possibly because of the presence of impurity phases and/or variations under the growth conditions. In contrast, the predicted increase in the Na concentration for AAC = 1.0 does not match the ~10 times higher Na content from our APT measurements on the Cu-free reference sample (see Figure 5), although the trend is correct on a qualitative level. A likely explanation for the discrepancy is that the maximum solubility is not reached during processing for this sample because much greater amount of Na from the substrate is required to saturate the absorber. Further analysis of this hypothesis from the perspective of alloy formation rather than the dilute limit approximation is provided below.
The observed trends in solubility versus AAC can be explained by a mismatch of ionic sizes of the group-I cations and alkali impurities. According to Shannon,59 crystal ionic radii of four-coordinated ions are 1.13 Å for Na\(^{1+}\), 1.51 Å for K\(^{1+}\), 0.74 Å for Cu\(^{1+}\), and 1.14 Å for Ag\(^{1+}\). As one can see, the Na\(^{1+}\) ion is considerably larger than Cu\(^{1+}\) but of the same size as Ag\(^{1+}\), suggesting that alk\(^{1+}\) induces less stress on the lattice and thus has lower formation energy (on average) in Ag-rich ACIGSe. The size mismatch increases for heavier alkalis, but it always remains smaller in Ag-based systems, resulting in a general tendency of increasing solubility with AAC.

To further explore the role of lattice stress and consider the alkali incorporation beyond the dilute limit, we also computed mixing enthalpies of (Na,Ag)InSe\(_2\), (Na,Cu)InSe\(_2\), (K,Ag)-InSe\(_2\), and (K,Cu)InSe\(_2\) alloys as

\[
\Delta H^{\text{mix}} = E_{\text{tot}}(\text{Alk}_x\text{Ag}_1-x\text{InSe}_2) - xE_{\text{tot}}(\text{AlkInSe}_2) - (1-x)E_{\text{tot}}(\text{AgInSe}_2)
\]

where \(E_{\text{tot}}\) represents computed total energies for supercells of different compositions. The Ga-based alloys were not considered because of the lack of structural information on NaGaSe\(_2\), which might be a sign of its instability. The alloy interaction (bowing) parameters for mixing enthalpies were extracted from parabolic fits to the computed energy values, as shown in Figure 7. Furthermore, the consolute temperatures (the points at which the alloys become fully miscible) were estimated from a regular solution approximation as \(T_c = \Omega/2k_B\). The obtained interaction parameters \(\Omega\) for the respective systems are 96.8, 367.3, 557.6, and 1043.8 meV/f.u. (per formula unit, which yield consolute temperatures of 288, 1858, 2962, and 5783 °C, in agreement with the earlier results for Cu-based chalcopyrites.15 As expected, the mixing enthalpies are lower in Ag-based systems because of the aforementioned smaller ionic size mismatch. This tendency was also observed for Rb and Cs, but the corresponding mixing parameters are not extracted because of severe relaxation experienced by the alkali-rich supercells. These consolute temperatures for all except (Na,Ag)InSe\(_2\) alloys are beyond the reach of synthesis as the chalcopyrite systems melt at lower temperatures.60 As such, the wide miscibility gap during processing clearly limits alkali solubility for most systems. However, the exception of (Na,Ag)InSe\(_2\) means that this alloy can form during absorber deposition (550 °C) as well as during the PDT (350 °C). Practically, it means that the solubility of Na in AgInSe\(_2\) absorbers is not thermodynamically limited but instead governed by the processing parameters (primarily time and temperature because of the thermally activated nature of Na in-diffusion from the substrate), as we hypothesized above. Considering that the dependence of Na\(_i\) formation energy on GGI (see Figure 6a) is weak, this conclusion can also be generalized to all AIGSe alloys, thereby explaining why the increase in the Na concentration in the Cu-free reference AIGSe sample deduced from the APT analysis was below the predicted equilibrium value.

4. CONCLUSIONS

In this work, we studied the relationship of Ag alloying in CIGSe on the alkali dispersion in bulk and at interfaces to better understand the enhancements in device performance related to the addition of Ag. Experimental analysis is performed for ACIGSe absorbers deposited on two different (K- and Na-rich) glass substrate types. The ion exchange mechanism commonly discussed in the literature for light and heavy alkali elements in CIGSe is observed for Na and K distributions in GBs and GLs. Alkali segregations at the CdS/ACIGSe and rear interfaces, as well as in the GBs, were detected. K segregation appears to dominate over Na at the GBs in CIGSe and ACIGSe. While this behavior can be expected with the HSG substrate, simply because more K is supplied, stronger Na segregations would be expected when using the SLG substrate if not for the ion exchange mechanism. At the same time, GLs contain greater concentrations of Na than K, even for the absorber grown on the HSG substrate. This indicates higher solubility of Na in GLs compared to K. Furthermore, it is found that the Na concentration in the GLs increases with Ag-alloying. The nanoscale experimental analysis was combined with first-principles calculations, providing strong indications of increased solubility of alkali elements in GLs of ACIGSe compared to CIGSe. Such a behavior stems from a mismatch of ionic sizes of group-I cations and alkali impurities, with Na\(^{1+}\) ions, for instance, being similar in size to Ag\(^{1+}\) but considerably larger than Cu\(^{1+}\), and hence, inflicting less stress upon formation of Na\(_i\) in Ag-alloyed CIGSe. The same rationale applied to heavier alkali elements as well. Hence, an increase in \(V_{\text{OC}}\) of CIGSe devices with the addition of Ag can be related to higher acceptance of alkali elements in the matrix, as well as improved band alignments and/or other factors discussed earlier. The fundamental difference in alkali dispersion demonstrated here for Ag-alloyed CIGSe absorbers should be taken into consideration when designing optimized alkali treatments in single- or multiple-junction solar cells using these types of absorbers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c20539.

Local chemical analysis of the CdS/ACIGSe interface; as-computed formation energies of Alk\(_i\) in ACIGSe supercells without additional processing with the CE formalism; defect formation energies assuming equilibrium between (Ag,Cu)(In,Ga)\(_3\)Se\(_5\) and ACIGSe with the same AAC and GGI ratios; and primitive cell used for simulation of (Ag,Cu)(In,Ga)\(_3\)Se\(_5\) (in CIF format) (PDF)

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REFERENCES

(1) Ramanujam, J.; Singh, U. C. Copper Indium Gallium Selenide Based Solar Cells – a Review. Energy Environ. Sci. 2017, 10, 1306–1319.
(2) Guillemoles, J. F. The Puzzle of Cu(In,Ga)Se2 (CIGS) Solar Cells Stability. Thin Solid Films 2002, 403–404, 405–409.
(3) Gloeckler, M.; Sites, J. R. Band-Gap Grading in Cu(In,Ga)Se2 Solar Cells. J. Phys. Chem. Solids 2005, 66, 1891–1894.
(4) Povalla, M.; Paetel, S.; Ahlswede, E.; Wuerz, R.; Wessendorf, C. D.; Majstoran Friedmeier, T. Thin-Film Solar Cells Exceeding 22% Solar Cell Efficiency: An Overview on CdTe, Cu(In,Ga)Se2, and Perovskite-Based Materials. Appl. Phys. Rev. 2018, 5, 041602.
(5) Wei, S. H.; Zanger, A. Band Offsets and Optical Bowings of Chalcopyrites and Zn-Based II-VI Alloys. J. Appl. Phys. 1995, 78, 3846–3856.
(6) Han, G. M.; Boyle, J. H.; Shafarman, W. N. Characterization and Device Performance of (AgCu)(InGa)2 Absorber Layers. 2009 34th IEEE Photovoltaics Specialists Conference, Philadelphia, PA, 2009; pp 001240–001245.
(7) Boyle, J. H.; McCandless, B. E.; Shafarman, W. N.; Birkmire, R. W. Structural and Optical Properties of (AgCu)(InGa)2 Polycrystalline Thin Film Alloys. J. Appl. Phys. 2014, 115, 223504.
(8) Keller, J.; Sophia, K. V.; Stolt, O.; Stolt, L.; Persson, C.; Scragg, J. J. S.; Törnadal, T.; Edoff, M. Wide-Gap (AgCu)(InGa)2 Solar Cells with Different Buffer Materials — A Path to a Better Heterojunction. Prog. Photovoltaics 2020, 28, 237–250.
(9) Shafarman, W.; Thompson, C.; Boyle, J.; Hanket, G.; Erslev, P.; Cohen, J. D. Device Characterization of (AgCu)(InGa)2 Solar Cells. 2010 35th IEEE Photovoltaics Specialists Conference, Honolulu, HI, 2010; pp 325–329.
(10) Edoff, M.; Jarmar, T.; Nilsson, N. S.; Wallin, E.; Hogstrom, D.; Stolt, O.; Lundberg, O.; Shafarman, W.; Stolt, L. High VOC in (CuAg)(In,Ga)Se2 Solar Cells. IEEE J. Photovoltaics 2017, 7, 1789–1795.
(11) Kim, K.; Park, J. W.; Yoo, J. S.; Cho, J.-s.; Lee, H.-D.; Yun, J. H. Ag Incorporation in Low-Temperature Grown Cu(In,Ga)Se2 Solar Cells Using Ag Precursor Layers. Sol. Energy Mater. Sol. Cells 2016, 146, 114–120.
(12) Kim, K.; Ahn, S. K.; Choi, J. H.; Yoo, J.; Eo, Y.-J.; Cho, J.-S.; Cho, A.; Gwak, J.; Song, S.; Cho, D.-H.; Chung, Y.-D.; Yun, J. H. Highly Efficient Ag-Alloyed Cu(In,Ga)Se2 Solar Cells with Wide Bandgaps and Their Application to Chalcopyrite-Based Tandem Solar Cells. Nano Energy 2018, 48, 345–352.
(13) Chen, L.; Lee, J.; Shafarman, W. N. The Comparison of (Ag,Cu)(In,Ga)Se2 and Cu(In,Ga)Se2 Thin Films Deposited by Three-Stage Coevaporation. IEEE J. Photovoltaics 2014, 4, 447–451.
(14) Sun, Y.; Lin, S.; Li, W.; Cheng, S.; Zhang, Y.; Liu, Y.; Liu, W. Review on Alkali Element Doping in Cu(In,Ga)Se2 Thin Films and Solar Cells. Engineering 2017, 3, 452–459.
(15) Siebentritt, S.; Avancini, E.; Bär, M.; Bombsch, J.; Bourgeois, E.; Buecheler, S.; Carron, R.; Castro, C.; Duguay, S.; Félix, R.; Handick, E.; Hariskos, D.; Havu, V.; Jackson, P.; Komsa, H. P.; Kunze, T.; Malitckaya, M.; Menozzi, R.; Nesladek, M.; Nicoara, N.; Puska, M.; Raghuvanshi, M.; Pareige, P.; Sadowasser, S.; Sozzi, G.; Tiwari, A. N.; Ueda, S.; Vilalta-Clemente, A.; Weiss, T. P.; Werner, F.; Wilks, R. G.; Witte, W.; Wolter, M. H. Heavy Alkali Treatment of Cu(In,Ga)Se2 Solar Cells: Surface versus Bulk Effects. Adv. Energy Mater. 2020, 10, 1903752.
(16) Granath, K.; Bodegård, M.; Stolt, L. Effect of NaF on Cu(In,Ga)Se2 Thin Film Solar Cells. Sol. Energy Mater. Sol. Cells 2000, 60, 279–293.
(17) Buecheler, S.; Tiwari, A. N. Unveiling the Effects of Post-Deposition Doping of Alkali Metals on Cu(In,Ga)Se2 Thin Films. Sol. Energy Mater. Sol. Cells 2017, 120, 539–548.
(18) Kronik, L.; Cahen, D.; Stolk, H. W. Effects of Sodium on Polycrystalline Cu(In,Ga)Se2 and Its Solar Cell Performance. Adv. Mater. 1998, 10, 31–36.
(19) Muzzillo, C. P.; Poplawsky, J. D.; Tong, H. M.; Guo, W.; Anderson, T. Revealing the Beneficial Role of K in Grain Interiors, Grain Boundaries, and at the Buffer Interface for Highly Efficient CuInSe2 Solar Cells. Prog. Photovoltaics 2018, 26, 825–834.
(20) Malitckaya, M.; Komsa, H.-F.; Havu, V.; Puska, M. J. Effect of Alkali Metal Atom Doping on the CuInSe2-Based Solar Cell Absorber. J. Phys. Chem. C 2017, 121, 15516–15528.
(21) Wuerz, R.; Hempel, W.; Jackson, P. Diffusion of Rb in Polycrystalline Cu(In,Ga)Se2 Layers and Effect of Rb on Solar Cell Parameters of Cu(In,Ga)Se2 Thin-Film Solar Cells. J. Appl. Phys. 2018, 124, 165305.
(22) Muzzillo, C. P. Review of Grain Interior, Grain Boundary, and Interface Effects of K in CIGS Solar Cells: Mechanisms for Performance Enhancement. Sol. Energy Mater. Sol. Cells 2017, 172, 18–24.
(23) Yuan, Z.-K.; Chen, S.; Xie, Y.; Park, J.-S.; Xiang, H.; Gong, X.-G.; Wei, S.-H. Na-Diffusion Enhanced p-Type Conductivity in Cu(In,Ga)Se2: A New Mechanism for Efficient Doping in Semiconductors. Adv. Energy Mater. 2016, 6, 1601191.
(24) Pianezi, F.; Reinhardt, P.; Chirilă, A.; Bissig, B.; Nishiwaki, S.; Buecheler, S.; Tiwari, A. N. Unveiling the Effects of Post-Deposition Treatment with Different Alkaline Elements on the Electronic Properties of CIGS Thin Film Solar Cells. Phys. Chem. Chem. Phys. 2014, 16, 8843–8851.
(25) Urbaniak, A.; Igalson, M.; Pianezi, F.; Bücheler, S.; Chirilă, A.; Reinhardt, P.; Tiwari, A. N. Effects of Na Incorporation on Electrical
Properties of Cu(In,Ga)Se₂-Based Photovoltaic Devices on Polyimide Substrates. Sol. Energy Mater. Sol. Cells 2014, 128, 52–56.

(26) Donzel-Gargard, O.; Larsson, F.; Törndahl, T.; Stolt, L.; Eddo, M. Secondary Phase Formation and Surface Modification from a High Dose KE Post Deposition Treatment of Ag,Cu(In,Ga)Se₂ Solar Cell Absorbers. Prog. Photovoltaics 2019, 27, 220–228.

(27) Larsson, F.; Donzel-Gargard, O.; Keller, J.; Eddo, M.; Törndahl, T. Atomic Layer Deposition of Zn(O,S) Buffer Layers for Cu(In,Ga)Se₂ Solar Cells with KE Post Deposition Treatment. Sol. Energy Mater. Sol. Cells. 2018, 183, 8–15.

(28) Feurer, T.; Fu, F.; Weiss, T. P.; Avancini, E.; Löckinger, J.; Buecheler, S.; Tiwari, A. N. RF Post Deposition Treatment for Narrow Bandgap Cu(In,Ga)Se₂ Solar Cells. Thin Solid Films 2019, 670, 34–40.

(29) Caballero, R.; Kaufmann, C. A.; Eisenbarth, T.; Unold, T.; Klenk, R.; Schock, H.-W. High Efficiency Low Temperature Grown Cu(In,Ga)Se₂ Thin Film Solar Cells on Flexible Substrates Using NaF Precursor Layers. Prog. Photovoltaics 2011, 19, 547–551.

(30) Valdes, N. H.; Jones, K. J.; Opila, R. L.; Shafarman, W. N. Influence of Ga and Ag on the KE Post Treatment Chemistry for CIGS Solar Cells. IEEE J. Photovoltaics 2019, 9, 1846–1851.

(31) Valdes, N. H.; Lee, J.; Shafarman, W. N. Ag Alloying and KE Treatment Effects on Low Bandgap CIGS Solar Cells. IEEE J. Photovoltaics 2019, 9, 906–912.

(32) Raghuvanshi, M.; Thöner, B.; Soni, P.; Wittig, M.; Wuerz, R.; Cojocaru-Mirédin, O. Evidence of Enhanced Carrier Collection in Cu(In,Ga)Se₂ Grain Boundaries: Correlation with Microstructure. ACS Appl. Mater. Interfaces 2018, 10, 14759–14766.

(33) Schwarz, T.; Stechmann, G.; Gault, B.; Cojocaru-Mirédin, O.; Choi, P.; Redinger, A.; Siebentritt, S.; Raabe, D. Correlative Transmission EBSD-APT Analysis of Grain Boundaries in Cu(In,Ga)Se₂ and CuZnSnSe₄ Based Thin-Film Solar Cells. Microsc. Microanal. 2017, 23, 672–673.

(34) Colombara, D.; Werner, F.; Schwarz, T.; Cañiero Infante, L.; Fleming, Y.; Valle, N.; Spindler, C.; Vaccieri, E.; Rey, G.; Guennou, M.; Bouttemy, M.; Anjon, A. G.; Perel Alason, I.; Melchiorre, M.; El Adib, B.; Gault, B.; Raabe, D.; Dale, P. J.; Siebentritt, S. Sodium Enhances Indium-Gallium Interdiffusion in Copper Indium Gallium (In,Ga)Se₂ and CuZnSnSe₄ Based Thin-Film Solar Cells. J. Mater. Microanal. 2017, 29, 2017–2022.

(35) Choi, P.-P.; Cojocaru-Mirédin, O.; Wuerz, R.; Raabe, D. Comparative Atom Probe Study of Cu(In,Ga)Se₂ Thin-Film Solar Cells Deposited on Soda-Lime Glass and Mild Steel Substrates. J. Appl. Phys. 2011, 110, 124513.

(36) Keller, J.; Schlesiger, R.; Riedel, I.; Parisi, J.; Schmitz, G.; Avellan, A.; Dalibor, T. Grain Boundary Investigations on Sulfurized Cu(In,Ga,Se)₂ Solar Cells Using Atom Probe Tomography. Sol. Energy Mater. Sol. Cells. 2013, 117, 592–598.

(37) Cojocaru-Mirédin, O.; Choi, P.; Wuerz, R.; Raabe, D. Atomic-Scale Distribution of Impurities in CuInSe₂-Based Thin-Film Solar Cells. Ultramicroscopy 2011, 111, 552–556.

(38) Vilalta-Clemente, A.; Raghuvanshi, M.; Duguay, S.; Castro, C.; Cadel, E.; Pareige, P.; Jackson, P.; Wuerz, R.; Harisoks, D.; Witte, W. Rubidium Distribution at Atomic Scale in High Efficient Cu(In,Ga,Se)₂ Thin-Film Solar Cells. Appl. Phys. Lett. 2018, 112, 103105.

(39) Cojocaru-Mirédin, O.; Choi, P.-P.; Abou-Ras, D.; Schmitz, S. J.; Cadel, E.; Rabe, D. Characterization of Grain Boundaries in Cu(In,Ga,Se)₂ Films Using Atom-Point Tomography. IEEE J. Photovoltaics 2011, 1, 207–212.

(40) Cojocaru-Mirédin, O.; Schwarz, T.; Abou-Ras, D. Assessment of Elemental Distributions at Line and Planar Defects in Cu(In,Ga)-Se Thin Films by Atom Probe Tomography. Scr. Mater. 2018, 148, 106–114.

(41) Cadel, E.; Barreau, N.; Kessler, J.; Pareige, P. Atom Probe Study of Sodium Distribution in Polycrystalline Cu(In,Ga)Se₂ Thin Film. Acta Mater. 2010, 58, 2634–2637.

(42) Stokes, A.; Al-Jassim, M.; Diercks, D.; Clarke, A.; Gorman, B. Impact of Wide-Ranging Nanoscale Chemistry on Band Structure at Cu(In, Ga)Se₂ Grain Boundaries. Sci. Rep. 2017, 7, 14163.
Overall Distribution of Rubidium in Highly Efficient Cu(In,Ga)Se₂ Solar Cells. ACS Appl. Mater. Interfaces 2018, 10, 40592–40598.

(63) Rau, U.; Taretto, K.; Siebentritt, S. Grain Boundaries in Cu(In,Ga)(Se,S)₂ Thin-Film Solar Cells. Appl. Phys. A: Mater. Sci. Process. 2009, 96, 221–234.

(64) Persson, C.; Zunger, A. Anomalous Grain Boundary Physics in Polycrystalline CuInSe₂: The Existence of a Hole Barrier. Phys. Rev. Lett. 2003, 91, 266401.

(65) Hellman, O. C.; Seidman, D. N. Measurement of the Gibbsian Interfacial Excess of Solute at an Interface of Arbitrary Geometry Using Three-Dimensional Atom Probe Microscopy. Mater. Sci. Eng., A 2002, 327, 24–28.

(66) Grini, S.; Sopiha, K. V.; Ross, N.; Liu, X.; Bjørheim, T. S.; Platzer-Björkman, C.; Persson, C.; Vines, L. Strong Interplay between Sodium and Oxygen in Kesterite Absorbers: Complex Formation, Incorporation, and Tailoring Depth Distributions. Adv. Energy Mater. 2019, 9, 1900740.

(67) Grini, S.; Aboulfadl, H.; Ross, N.; Persson, C.; Platzer-Björkman, C.; Thuvander, M.; Vines, L. Dynamic Impurity Redistributions in Kesterite Absorbers. Phys. Status Solidi B 2020, 257, 2000062.

(68) Chirila, A.; Reinhard, P.; Pianezzi, F.; Bloesch, P.; Uhl, A. R.; Fella, C.; Kranz, L.; Keller, D.; Gretener, C.; Hagendorfer, H.; Jaeger, D.; Erni, R.; Nishiwaki, S.; Buecheler, S.; Tiwari, A. N. Potassium-Induced Surface Modification of Cu(In,Ga)Se₂ Thin Films for High-Efficiency Solar Cells. Nat. Mater. 2013, 12, 1107–1111.

(69) Jackson, P.; Wuerz, R.; Hariskos, D.; Lotter, E.; Witte, W.; Powalla, M. Effects of Heavy Alkali Elements in Cu(In,Ga)Se₂ Solar Cells with Efficiencies up to 22.6%. Phys. Status Solidi RRL 2016, 10, 583–586.

(70) Erslev, P. T.; Lee, J.; Hanket, G. M.; Shaferman, W. N.; Cohen, J. D. The Electronic Structure of Cu(In₁₋ₓGax)Se₂ Alloyed with Silver. Thin Solid Films 2011, 519, 7296–7299.

(71) Prota, T. J.; Strennen, S.; Olson, D.; Lawrence, D.; Larson, D. J. A Study of Parameters Affecting Atom Probe Tomography Specimen Survivability. Microsc. Microanal. 2019, 25, 425–437.

(72) Persson, C.; Zhao, Y. J.; Lany, S.; Zunger, A. N-Type Doping of CuInSe₂ and CuGaSe₂. Phys. Rev. B: Condens. Matter Mater. Phys. 2005, 72, 035211.

(73) Sopiha, K. V.; Larsen, J. K.; Donzel-Gargand, O.; Khavari, F.; Keller, J.; Edoff, M.; Platzer-Björkman, C.; Persson, C.; Scragg, J. J. S. Thermodynamic Stability, Phase Separation and Ag Grading in (Ag,Cu)(In,Ga)Se₂ Solar Absorbers. J. Mater. Chem. A 2020, 8, 8740–8751.

(74) Hariskos, D.; Powalla, M. Thermodynamic Limitations for Alkali Metals in Cu(In,Ga)Se₂. J. Mater. Res. 2017, 32, 3789–3800.

(75) Chen, J.; Shen, H.; Zhai, Z.; Liu, F.; Zhu, Z.; Luo, M. Performance and Stability Enhancement of Cu(InGa)Se₂ Solar Cells on Ultrathin Glass by Potassium Incorporation. Mater. Lett. 2020, 271, 127749.

(76) Taguchi, N.; Tanaka, S.; Ishizuka, S. Direct Insights into RbInSe₂ Formation at Cu(In,Ga)Se₂ Thin Film Surface with RbF Postdeposition Treatment. Appl. Phys. Lett. 2018, 113, 113903.

(77) Lin, T.-Y.; Khatri, I.; Matsuura, J.; Shudo, K.; Huang, W.-C.; Sugiyama, M.; Iai, C.-H.; Nakada, T. Alkali-Induced Grain Boundary Reconstruction on Cu(In,Ga)Se₂ Thin Film Solar Cells Using Cesium Fluoride Post Deposition Treatment. Nano Energy 2020, 68, 104299.

(78) Muzzillo, C. P.; Mansfield, L. M.; Ramanathan, K.; Anderson, T. J. Properties of Cu₁₋ₓKₓInSe₂ Alloys. J. Mater. Sci. 2016, 51, 6812–6823.

(79) Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. 1976, 32, 751–767.

(80) Kühn, G.; Möller, W.; Engel, W. Heats and Entropies of Fusion of ABC2 Chalcocypite Semiconductors. Thermochim. Acta 1984, 78, 129–134.