Chemistry of K in Cu(In,Ga)Se₂ photovoltaic absorbers: effects of temperature on Cu-K-In-Se films

Christopher P. Muzzillo,^{1,2} Ho Ming Tong,^{2,3} and Tim Anderson²

¹National Renewable Energy Laboratory, Golden, CO 80401, USA

²Department of Chemical Engineering, University of Florida, Gainesville, FL 32611, USA

³Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

Abstract

Incorporation of K has led to world record Cu(In,Ga)Se₂ photovoltaic power conversion efficiencies, but there is poor consensus about the role of phase impurities in these advances. This work lays a foundation for identifying and controlling these phase impurities. Films of Cu-K-In-Se were co-evaporated at varied K/(K+Cu) compositions and substrate temperatures (with constant (K+Cu)/In ~ 0.85). Increased Na composition on the substrate's surface and decreased growth temperature were both found to favor Cu_{1-x}K_xInSe₂ alloy formation, relative to two-phase CuInSe₂+KInSe₂ formation. Structures from X-ray diffraction (XRD), band gaps, resistivities, minority carrier lifetimes and carrier concentrations from time-resolved photoluminescence were in agreement with previous reports, where low K/(K+Cu) composition films exhibited properties promising for photovoltaic absorbers. Films grown at 400-500°C were then annealed to 600°C in a controlled Se ambient, which caused K loss by evaporation in proportion to the initial K/(K+Cu) composition. Similar to growth temperature, annealing drove Cu_{1-x}K_xInSe₂ alloy consumption and CuInSe₂+KInSe₂ production, as evidenced by high temperature XRD. Annealing also decomposed KInSe₂ and formed K₂In₁₂Se₁₉. At high temperature, the KInSe₂

crystal lattice gradually contracted as temperature and time increased, as well as just time. Evaporative loss of K during annealing could accompany the generation of vacancies on K lattice sites, and may explain the KInSe₂ lattice contraction. This knowledge of Cu-K-In-Se material chemistry may be used to predict and control minor phase impurities in Cu(In,Ga)(Se,S)₂ photovoltaic absorbers—where impurities below typical detection limits may have played a role in recent world record photovoltaic efficiencies that utilized KF post-deposition treatments.

Graphical abstract:

Keywords: Photovoltaics; Solar cells; Semiconductors; Phase transformation; Thin films; Physical vapor deposition

1. Introduction

Recent reports have detailed power conversion efficiency enhancement when potassium fluoride and selenium have been co-evaporated onto Cu(In,Ga)(Se,S)_2 (CIGS) absorbers at around 350°C (KF post-deposition treatment (PDT)) [1-25]. In particular, 6 of the last 8 world record CIGS efficiencies have employed a KF PDT [1, 3, 4, 11, 26, 27], ultimately advancing the record efficiency from 20.3 to 22.6% in under 4 yr. KF PDT successes in the laboratory have now been extended to commercially-relevant chalcogenized Cu(In,Ga)(Se,S)_2 absorbers [11], full size (0.75 m^2) modules [12], and Cd-free Zn(O,S) buffers [2, 11, 16, 28]. Although the mechanisms responsible for these efficiency improvements are not clear, the KF PDT has been associated with many phenomena. As example this treatment is reported by several researchers to increase hole concentration [5-7, 10, 13-19, 29-31] by consuming In_{Cu} compensating donors to produce K_{Cu} neutral defects [32], but in contrast, other researchers have indicated decreased hole concentration via reduction of Na_{Cu} , which produces In_{Cu} compensating donors [1, 7, 9, 20, 33]. Other examples of the effect of KF PDTs include Na depletion or formation of soluble Na compounds [1, 5-7, 9, 10, 12, 13, 17, 21-23, 30, 34, 35], Ga depletion at the top surface [1, 7, 9, 12-14, 21, 22, 24, 34, 36-38], Cu depletion at the top surface [6, 12, 14, 24, 25, 39] resulting in better near-surface inversion [1, 7, 9, 20, 40] or decreased valence band energy [13, 19-21, 24, 29, 36, 38, 41], grain boundary passivation [5, 11, 42], general defect passivation [2, 3, 10, 11], minority carrier lifetime enhancement [8, 14, 17-19], morphology changes resulting in increased CdS nucleation sites [2, 9, 43] as well as general changes in CdS growth [13, 19, 21, 36, 39, 40, 44], formation of a passivating K-In-Ga-Se [9, 45] or K-In-Se [13, 19, 21, 36-38, 44] interfacial

compound, formation of a current blocking interfacial compound [30, 46], formation of elemental Se at the surface [13, 37], formation of surface Cu_{2-x}Se and GaF_3 [13], consumption of a surface 'ordered vacancy compound' [13], and decreased trap concentration [34]. Substrate surfaces with high K content also led to increased carrier concentrations [15, 32, 47] and modified Cu-Ga-In interdiffusion [15, 47, 48]. Lepetit et al. co-evaporated KF, In, and Se onto CIGS, forming either KInSe_2 or K-doped amorphous In_2Se_3 , and achieved results similar to a KF PDT [37]. A PDT without KF (just Se) has also been shown to significantly alter CIGS absorber properties [49, 50], confounding the conclusions of KF PDT comparisons. High absorber Na and K composition has also been linked to accelerated degradation in photovoltaic (PV) performance [51], which may undermine the relevance of initial performance gains achieved with high Na and K levels. Specifically, Na and K diffused into and degraded the ZnO layer after 100 h in damp heat and light [51]. This result underscores the importance of understanding the materials chemistry of alkali metal bonding in CIGS and contacting materials.

While the detailed mechanisms underlying the observed effects of KF PDTs remain uncertain, it has been established that a significant amount of K segregates at the heterojunction in the most efficient solar cells [1]. These advances have heightened interest in Cu-K-In-Se material with K-rich ($\text{K}/(\text{K}+\text{Cu}) > 0.30$) and group I-poor compositions (i.e. $(\text{K}+\text{Cu})/\text{In} \sim 0.85$, which avoids Cu_2Se). In a departure from work utilizing KF precursors and PDTs, Cu, KF, In, and Se were co-evaporated to form $\text{Cu}_{1-x}\text{K}_x\text{InSe}_2$ (CKIS) alloys with $x=\text{K}/(\text{K}+\text{Cu})$ varied from 0 to 1 [35, 52, 53]. Increasing x in CKIS was found to monotonically decrease the chalcopyrite lattice parameter, increase the band gap, and increase the apparent carrier concentration. Moderate K compositions ($0 < x < 0.30$) exhibited significantly longer minority carrier lifetimes [52, 53], relative to $x \sim 0$ and $x \geq 0.30$. Superior PV performance was also observed at $x \sim 0.07$

for a Ga-alloyed film with $\text{Ga}/(\text{Ga}+\text{In}) \sim 0.3$ [10]. The Na composition at the substrate surface was also found to influence the amount of CKIS alloy formation during growth, relative to mixed-phase $\text{CuInSe}_2 + \text{KInSe}_2$ formation [35]. Those studies are extended in the present work to detail the constitution of the deposited film as a function of overall composition and temperature in the Cu-K-In-Se system at compositions of interest for PV applications. KF PDTs lead to very thin chemically modified layers that are difficult to characterize and may lead to non-reproducibility. In contrast, the present work used temperature to affect changes in films that were easily observable with basic characterization—providing insight into Cu-K-In-Se chemistry. The conclusions drawn in this work have been utilized in subsequent papers to explain phenomena in highly efficient $\text{Cu}_{1-x}\text{K}_x\text{InSe}_2$ [54] and $\text{Cu}_{1-x}\text{K}_x\text{In}_{1-y}\text{Ga}_y\text{Se}_2$ [55] solar cells, confirming the usefulness of the present materials chemistry study.

2. Experimental

Most CIGS films are grown with $\text{Ga}/(\text{Ga}+\text{In}) \sim 0.2 - 0.3$ and intentional cation composition gradients [1, 56, 57]. In this study, however, Ga has been excluded to simplify data interpretation. A constant rate, single temperature process was also chosen to achieve uniformity in depth and avoid compositional gradients, as K [15, 47] and Na [58, 59] have been shown to affect cation diffusion in CIGS. Co-evaporation of Cu, KF, In, and Se was performed on SLG and SLG/Mo ("Mo") substrates at 400°C, 500°C, or 600°C, as previously detailed [53]. The group I to III cation atomic ratio, $(\text{K}+\text{Cu})/\text{In}$, in the film was maintained near 0.85 for all depositions, while x was varied between 0 and 1. Deposited film composition was measured with X-ray fluorescence (XRF; Fischerscope X-ray XDV-SDD with a W anode, 10 μm Ni filter, and silicon drift detector), secondary ion mass spectrometry (SIMS), and energy dispersive X-ray

spectroscopy (EDS on a transmission electron microscope). As noted [53], peak overlap between K and In reduces the certainty of XRF and EDS composition measurement, thus film compositions from in situ electron impact emission spectroscopy (EIES) and quartz crystal microbalance data were used unless otherwise noted. Interference between $^{39}\text{K}^{41}\text{K}^+$ and $^{80}\text{Se}^+$ ions was observed during SIMS measurements on films with high K content ($x \geq 0.38$), so $^{76}\text{Se}^+$ ions were used to determine the Se composition. Symmetric X-ray diffraction (XRD) was performed with a Rigaku Ultima IV diffractometer to determine structure and assist in phase identification, as previously reported [53]. Standard diffraction patterns were calculated from published phase structures [53, 60, 61]. Film morphology was observed using scanning electron microscopy (SEM). Ultraviolet-visible (UV-visible) spectroscopy was performed to measure transmissivity and reflectivity of SLG/Cu-K-In-Se samples using a Cary 5000 spectrophotometer with a diffuse reflectance-integrating sphere. Film thicknesses were measured with a Dektak 8 profilometer.

Through-film resistivity was measured with SLG/Mo/CKIS/Ni structures. Electron-beam evaporation of ~ 50 nm Ni, followed by ~ 3 μm Al through ~ 1.5 mm^2 apertures (normally used for solar cell grids) formed top contacts for current-voltage (IV) measurements, which were performed on a temperature-controlled stage at 25°C . Room temperature time-resolved photoluminescence (TRPL) was performed on absorber films with a 905 nm laser (1.37 eV) under low-injection conditions, and the response was detected with a near-infrared photomultiplier tube responsive to photons in the range 0.92 to 1.31 eV. A detailed description of the fiber optic system was published elsewhere [62]. Peak TRPL signals were used to estimate majority carrier concentrations by assuming a constant radiative coefficient for all samples, and single exponential functions were fitted to decays curves to estimate minority carrier lifetimes.

Phase changes and reactions were followed as a function of time and temperature in situ using high temperature XRD (HTXRD). In these experiments, a co-evaporated film was placed in a SiC-coated graphite chamber fitted with Al windows to allow heating along with elemental Se. The chamber was heated up to 600°C while symmetric HTXRD was performed. Temperature was increased in increments of 10 or 20°C, followed by 8 min XRD scans at constant temperature. For dwells, the temperature was rapidly ramped (100°C/min) to the set point, and held for the duration of the scans. Films were annealed in vacuum (base pressure $< 3 \times 10^{-6}$ Torr) by supplying evaporated Se, heating at 100°C/min to 600°C, then holding for 10 - 80 min, and finally cooling at 20°C/min to room temperature. The anneals were performed at 600°C to affect changes in the films grown at 400°C and 500°C that would be easily observable, and the HTXRD data provided additional insight into what would occur at other annealing temperatures.

3. Results

3.1. Effect of growth temperature

The substrate surface's Na content determined the extent of CKIS alloy formation [35]. High and low Na substrates were therefore employed to study the effect of temperature.

3.1.1. High Na substrates (SLG)

Baseline films of nominally CuInSe_2 ($x \sim 0$) were grown at 500°C for comparative purposes. These absorbers had narrower, more intense XRD peaks and more precipitous absorptivity onsets by UV-visible spectroscopy, relative to films grown at 400°C (not shown). These results are consistent with enhanced crystallinity at higher growth temperature. In addition

the CuInSe_2 films did *not* exhibit shifts in either XRD peak positions or band gap energies with growth temperature.

Films of Cu-K-In-Se with group I composition $x \sim 0.38$ were grown on SLG substrates at 500 and 600°C. The 500°C film was homogenous and exhibited a finer grain structure, suggesting an increased nucleation rate at the lower deposition temperature relative to the 600°C film (Fig. 1). On the other hand, the 600°C film exhibited segregation of large, planar crystals (right of Fig. 1; marked with yellow arrows). These precipitates appeared to be KInSe_2 , based on previous reports of SEM, XRD, and UV-visible spectroscopy on KInSe_2 films [53], and SEM/EDS on 2-phase $\text{CuInSe}_2 + \text{KInSe}_2$ films [35]. The differences between films grown on SLG at 500 and 600°C were similar to those between SLG and Mo substrates previously reported at 500°C [35], where low temperature and high Na favored CKIS alloy growth. Films were also grown with $x \sim 0.57$, and room temperature XRD patterns of the CKIS film grown at 500°C revealed that the CKIS alloy formation reaction was complete (Fig. 2), as inferred from chalcopyrite lattice parameter reduction (from 5.770 to 5.725 Å [53]). The 600°C film revealed reflections consistent with chalcopyrite $x \sim 0$ (CuInSe_2), as well as $\text{K}_2\text{In}_{12}\text{Se}_{19}$ and KInSe_2 . The XRD results were corroborated by UV-visible spectroscopy. Specifically, the 500°C film had a weak absorptivity onset that was nonlinear in the Tauc plot, and yielded a band gap of 1.28 ± 0.06 eV (Fig. S1), as expected for a CKIS film with $x \sim 0.57$ [53]. The 600°C film had two absorptivity transitions, which were linear in the Tauc plot, and yielded band gap values of 0.90 ± 0.05 eV and 2.50 ± 0.04 eV, which are similar to those for CuInSe_2 and KInSe_2 (1.05 and 2.71 eV [53]). The nonlinearity in the 500°C film reduced the certainty of its band gap, and the 600°C film's mixed phases violated the assumptions for extrapolating band gap with a Tauc plot, so these values are considered approximate.

Fig. 1. Plan view (top and middle) and cross-sectional (bottom) SEM micrographs of Cu-K-In-Se films with $x \sim 0.38$ grown on SLG at 500°C (left) and 600°C (right). KInSe₂ crystals are marked by yellow arrows.

Fig. 2. Room temperature symmetric XRD patterns from Cu-K-In-Se films with $x \sim 0.57$ grown on SLG at 600°C (top; red) and 500°C (bottom; black), with magnified (112), (204)/(220), and (116)/(312) peak ranges above. CuInSe_2 , CKIS, $\text{K}_2\text{In}_{12}\text{Se}_{19}$, and KInSe_2 peaks are indicated by red diamonds, green circles, orange up triangles, and purple down triangles, respectively. The CKIS peak positions correspond to a composition of $x \sim 0.57$ [53].

Fig. S1. (a) Absorptivity, α , and (b) Tauc plot, $(\alpha h\nu)^2$ versus photon energy for Cu-K-In-Se with $x \sim 0.57$ grown on SLG at 500°C (black circles) and 600°C (red triangles). Example least squares fits (green lines in (b) and (b) inset) extrapolated to 1.28 ± 0.06 , 0.90 ± 0.05 , and 2.50 ± 0.04 eV.

3.1.2. Low Na substrates (Mo)

The use of Mo substrates was previously shown to establish 3x less Na in the growing Cu-K-In-Se films by SIMS, relative to SLG substrates [35]. The effect of temperature on Na-deficient growth was studied for Cu-K-In-Se films with $x \sim 0$ and 0.38 on Mo at 400°C and 500°C. The $x \sim 0$ film exhibited enhanced crystallinity at higher growth temperature, but no XRD peak shifts (not shown). Fig. 3 collects typical cross-sectional and plan-view SEM images of films with $x \sim 0.38$ grown at 400°C and 500°C. The composition of the film grown at 500°C (Fig. 3, right) was determined by EDS as 20.5 ± 1.4 Cu, 10.6 ± 1.0 K, 18.1 ± 0.8 In, and 50.9 ± 2.0 Se (at. %) to give $x \sim 0.341 \pm 0.030$. This is in rough agreement with the values from in situ measurement (13.8 Cu, 8.6 K, 27.6 In, and 50.0 Se (at. %); $x \sim 0.376$). The film grown at 400°C (Fig. 3, left) was homogenous, and had a finer grain structure, relative to growth at 500°C (Fig. 3, right). This could relate to an increased nucleation rate, which would be expected at lower growth temperature. The 500°C film included large, planar KInSe₂ precipitates (right of Fig. 3; marked with yellow arrows). Films were also grown under the same conditions as those depicted in Fig. 3 but with higher K, $x \sim 0.57$. Similarly, the film grown at 400°C was completely alloyed CKIS, while the 500°C film was 2-phase CuInSe₂ + KInSe₂ (Fig. 4). Thus, changing growth temperature and substrate Na revealed very similar trends in phase growth [35]. The 400°C film had additional peaks at 17.9 and 29.6° 2 θ . These peaks were also observed in a similarly grown $x \sim 0.38$ film (not shown), only shifted to larger d-spacing. Previous reports on bulk

$\text{Cu}_{0.33}\text{K}_{0.67}\text{InSe}_2$ crystals found monoclinic symmetry [63, 64]. The new XRD peaks could relate to the structural transition from tetragonal CuInSe_2 to monoclinic $\text{Cu}_{0.33}\text{K}_{0.67}\text{InSe}_2$, warranting future study.

The resistivity of films grown on Mo at 400°C was measured for Mo/CKIS/Ni stacks with varied x composition. Increasing x decreased apparent resistivity at 0 V and in reverse bias (Fig. S2), and indicated a current blocking barrier for the Mo and/or Ni interface [53]. The resistivity of films grown at 400°C was larger than films grown at 500°C by roughly 2 decades [53], while the trends with composition changes were similar for each growth temperature. The correlation between apparent resistivity and K composition may therefore be unrelated to the intragranular properties of the CuInSe_2 , CKIS, or KInSe_2 crystals. As noted [53], some undetected grain boundary-segregated phase could dominate the apparent resistivity changes [65]. Bulk crystal resistivity measurements could help discern this effect. Films grown on Mo had superior lifetimes by TRPL, relative to SLG substrates. TRPL electron lifetimes and hole concentrations for Cu-K-In-Se films grown on Mo at 400°C, 500°C, and 600°C at different x compositions are compared in Fig. S3. Growth temperature and composition changed the phase constitution of the films and their semiconducting properties, so the mechanisms responsible for the trends in Fig. S3 are unclear. Further study with spectrally resolved TRPL would contribute to understanding the connections between improved lifetimes and CKIS alloy formation or consumption.

Fig. 3. Plan view (top) and cross-sectional (bottom) SEM micrographs of Cu-K-In-Se films with $x \sim 0.38$ grown on Mo at 400°C (left) and 500°C (right). KInSe₂ crystals are marked by yellow arrows.

Fig. 4. Room temperature symmetric XRD scans from Cu-K-In-Se films with $x \sim 0.57$ grown on Mo at 500°C (top; black) and 400°C (bottom; blue), with magnified (112), (204)/(220), and (116)/(312) peak ranges above. Mo, CuInSe₂, CKIS, and KInSe₂ peaks are labeled with black squares, red diamonds, green circles, and purple triangles, respectively. The CKIS peak positions correspond to a composition of $x \sim 0.57$ [53]. The question mark (?) denotes uncertainty in the peak assignment. 'β' and 'W' peaks are from Cu K_β and W impurity in the Cu radiation source.

Fig. S2. Apparent resistivity at 0 V bias (black circles) and -0.8 V bias (blue triangles) of Mo/CKIS/Ni versus in situ x composition of the CKIS. CKIS was grown at 400°C, and standard deviations from multiple contacts are shown as error bars.

Fig. S3. Minority carrier lifetime (a) and majority carrier concentration (b) from TRPL versus in situ x composition of the Cu-K-In-Se grown on Mo at 600°C (red plusses), 500°C (black circles), and 400°C (blue crosses).

The effect of growth parameters on the extent of the following net reaction was further solidified:

Switching from low to high Na substrates at 500°C was previously shown to favor the forward reaction. In this study, switching from high to low temperature was shown to further drive the reaction forward. Remarkably similar effects were observed for the following 3 process changes: from Mo to SLG at 500°C [35], from 600°C to 500°C on SLG (Fig. 1, 2, and S1), and from 500°C to 400°C on Mo (Fig. 3 and 4). These data were chosen to succinctly represent key features of a much larger dataset (for instance, 500°C and 400°C SLG data were similar, so the latter were excluded). Further study will be needed to determine the quantitative effects of Na and temperature, as well as the kinetic and/or thermodynamic origins of those effects. The effect of temperature was easily observed on samples with high K/(K+Cu) compositions. At lower K/(K+Cu) compositions, the magnitudes of lattice parameter and band gap shifts would make this effect difficult to observe with the presently employed methods. Future data on lower K/(K+Cu) compositions could help clarify the role of a potential CKIS miscibility gap in the presently observed phase transitions. Upon reversal of reaction (1), the CuInSe₂ precipitates could contain residual K, where measurements of K solubility in bulk chalcopyrite CIGS crystals would help characterize this.

3.2. Effect of annealing

Cu-K-In-Se films were grown on Mo and SLG substrates at 400 and 500°C, and were then annealed to 600°C for 10 - 80 min under vacuum. Regardless of substrate, deposition temperature, and annealing time, films exhibited more extensive growth of KInSe₂ crystals after annealing, as evidenced by SEM (e.g. Fig. S4; marked with a yellow arrow). XRD and UV-visible spectroscopy measurements both showed that as-deposited CKIS alloys decomposed into CuInSe₂ + KInSe₂ during anneals (Fig. S5 and S6), mirroring behavior at increased growth

temperature (Fig. 2, 4, and S1). K-In-Se ($x \sim 1$) films grown at 500°C predominantly contained KInSe_2 , although $\text{K}_2\text{In}_{12}\text{Se}_{19}$ impurities were often detected in XRD measurements at low intensity [53]. The band gap of $\text{K}_2\text{In}_{12}\text{Se}_{19}$ was determined to be 2.25 ± 0.02 eV by UV-visible spectroscopy (not shown), in qualitative agreement with its reported red appearance [66]. Annealing K-In-Se films to 600°C promoted partial decomposition of KInSe_2 and formation of $\text{K}_2\text{In}_{12}\text{Se}_{19}$ (Fig. S7). Subsequent humid air exposure caused spontaneous film delamination, preventing extensive characterization.

Fig. S4. Plan view (top) and cross-sectional (bottom) SEM micrographs of a Cu-K-In-Se film with $x \sim 0.38$ grown on SLG at 500°C (left) and then annealed at 600°C for 10 min (right). KInSe_2 crystals are marked by a yellow arrow.

Fig. S5. Room temperature symmetric XRD scans from a Cu-K-In-Se film with $x \sim 0.57$ grown on SLG at 500°C (bottom; black), and then annealed at 600°C for 10 min (top; red), with magnified (112), (204)/(220), and (116)/(312) peak ranges above. Peaks attributed to CuInSe_2 , CKIS, $\text{K}_2\text{In}_{12}\text{Se}_{19}$, and KInSe_2 are labeled with red diamonds, green circles, orange up triangles, and purple down triangles, respectively. The CKIS peak positions correspond to a composition of $x \sim 0.57$ [53]. 'β' and 'W' peaks are from $\text{Cu K}\beta$ and W impurity in the Cu radiation source.

Fig. S6. (a) Absorptivity, α , and (b) Tauc plot, $(\alpha h\nu)^2$, versus photon energy for CKIS with $x \sim 0.57$ grown on SLG at 500°C (black circles) and then annealed at 600°C for 10 min (red

triangles). Example least squares fits (green lines in (b) and (b) inset) extrapolated to 1.32 ± 0.06 , 0.86 ± 0.05 , and 2.71 ± 0.02 eV.

Fig. S7. Room temperature symmetric XRD scans from a K-In-Se film ($x \sim 1$) grown on SLG at 500°C (bottom; black), and then annealed at 600°C for 80 min (top; red). $\text{K}_2\text{In}_{12}\text{Se}_{19}$ and KInSe_2 peaks are labeled with orange up triangles and purple down triangles, respectively.

HTXRD directly probed the phase transitions as a function of temperature. In the first study, a CKIS alloy with $x \sim 0.57$ (grown at 400°C on SLG) was slowly heated to 600°C. Temperature was increased in 10 or 20°C increments, followed by constant temperature XRD scans (8 min each), and Fig. 5 shows their evolution. The sample initially showed reflections for only the CKIS alloy, but KInSe_2 peaks appeared in the 290 - 450°C temperature range. Near 410°C, the CKIS developed (204)/(220) texture (44.4° 2θ peak). At 430°C the background signal increased, possibly due to a phase transition or recrystallization (e.g. the $\text{L} \leftrightarrow \text{K}_2\text{Se} + \text{K}_2\text{Se}_2$ invariant reaction was reported near 430°C [67, 68]). In the temperature range 420 - 450°C the CKIS peaks abruptly shifted to larger d-spacing, and very intense KInSe_2 peaks simultaneously appeared. These changes are a result of reaction (1), and they corroborate previous studies [35,

52-55, 63, 64, 69] that found decreased apparent lattice parameters as x was increased in CKIS alloys, despite the larger atomic radius of K relative to Cu. The KInSe₂ peaks at 460°C corresponded to 1% larger a , b , and c lattice parameters. As the temperature step-ramp continued, however, the KInSe₂ lattice continuously compressed isotropically (i.e. peaks at greater 2θ displayed greater shifts). An unidentified peak shifted to smaller 2θ values in Fig. 5 (50° 2θ and 520°C).

Fig. 5. HTXRD temperature ramp for SLG/CKIS with $x \sim 0.57$ grown at 400°C. CuInSe₂, CKIS, and enlarged-lattice-KInSe₂ peaks are labeled with red diamonds, green circles, and purple triangles, respectively. The CKIS peak positions correspond to a composition of $x \sim 0.57$ [53]. The enlarged-lattice-KInSe₂ peaks were calculated with a 1% increase in the, b , and c lattice parameters. The question mark (?) denotes uncertainty in the peak assignment.

To better understand the origin of the peak shifts at high temperature observed in Fig. 5, two additional HTXRD experiments were performed on a K-In-Se film ($x \sim 1$; grown on SLG at 500°C): one with a rapid temperature ramp to 550°C followed by a series of isothermal scans, and a second temperature ramp. The dwell at 550°C (Fig. 6 (a)) also exhibited substantial peak shifts, indicative of a kinetic-limited reaction. The temperature ramp showed that the K₂In₁₂Se₁₉

+ KInSe_2 two-phase film recrystallized into KInSe_2 near 410 - 450°C (Fig. 6 (b)). The high temperature KInSe_2 peaks then shifted to smaller d-spacing as temperature and time increased, similar to the shifts of Fig. 5 and 6 (a). Other peaks shifted to smaller 2θ values in Fig. 6 (a) and (b) (near 31, 42, 50, 55, and 60° 2θ and 0 hr, and 32, 42, 50, 55, and 61° 2θ and 520°C, respectively), although the source of those shifts was unclear. The background increase near 230°C in Fig. 6 (b) could be a result of Se, which melts at 221°C. The background increase at 430°C in both Fig. 5 and 6 (b) may have emerged from a K-In-Se phase transition or recrystallization.

Fig. 6. HTXRD dwell at 550°C (a) and temperature ramp (b) for SLG/K-In-Se (i.e. $x \sim 1$) grown at 500°C. $\text{K}_2\text{In}_{12}\text{Se}_{19}$ and KInSe_2 peaks are labeled with orange up triangles and purple down triangles, respectively.

The XRF composition after vacuum anneals showed reduced K content for all $x > 0$, where more K loss occurred in films with greater initial K content (Fig. 7). A CuInSe_2 film ($x \sim 0$) contained more Na and K by SIMS after a 600°C anneal (Table 1) that is attributed to Na and

K out-diffusion from the substrate. However, the CKIS film with $x \sim 0.38$ showed substantially less K by SIMS after annealing (Na increased similar to the $x \sim 0$ case). The XRF and SIMS measurements demonstrated that K loss occurred during annealing, although residual K remained after 80 min anneals. As K loss occurred in addition to other phase transitions, any causal connection was unclear from the data.

Fig. 7. Change in K composition by XRF after annealing Cu-K-In-Se films at 600°C, plotted against in situ x composition. Films were grown at 400°C and 500°C, on SLG and Mo substrates, and annealed for 10, 20, or 80 min.

Table 1. Na and K SIMS signals integrated over the film and divided by thickness for Cu-K-In-Se films with in situ x of 0 and 0.38 grown at 500°C on Mo, and then annealed at 600°C for 10 min.

K/(K+Cu), or x	Sample	Na (cps/ μm)	K (cps/ μm)
0	Anneal	4.7×10^5	1.4×10^4
	500°C growth	1.6×10^4	4.6×10^3
0.38	Anneal	2.3×10^6	1.0×10^6
	500°C growth	7.0×10^5	3.0×10^6

The SEM, XRD, UV-visible spectroscopy, and HTXRD results on samples annealed under vacuum and atmospheric pressure resembled results for growth temperature, where high temperature annealing reversed reaction (1). Annealing additionally consumed KInSe₂ and produced K₂In₁₂Se₁₉. However, relative phase amounts of KInSe₂ and K₂In₁₂Se₁₉ were difficult to distinguish due to peak overlap in XRD (e.g. Fig. S5) and similar band gaps: 2.71 eV [52, 70] compared to 2.25 ± 0.02 eV, respectively. It was therefore unclear if the KInSe₂ decomposition and K₂In₁₂Se₁₉ formation was also driven by growth temperature, or just annealing. The combined XRF and SIMS results indicated that K loss occurred during the anneals. The reduction in K chemical potential during annealing achieved conditions *unlike* increasing growth temperature, as K chemical potential was held relatively constant in the latter.

Based on the combined XRD, UV-visible spectroscopy, HTXRD, XRF, and SIMS data, the following net reaction was favored at high temperature and reduced K chemical potential:

Here, the gaseous K-containing species was assumed to be K₂Se for the sake of illustration, as no K-Se vapor pressure data has been published. The KInSe₂ had (53-8)/(51-9)/(356)/(15-8) texture (60.5 - 63° 2θ peaks) in Fig. 5 and 6 (b), while it had (22-2)/(221) texture (23.7° 2θ peak) in Fig. 6 (a). However, the contraction of the KInSe₂ lattice at high temperature (Fig. 5, 6 (a), and 6 (b)) was apparently isotropic, so it may not stem from external stress. On the other hand, an isotropic reduction in KInSe₂ lattice volume may be expected for the following reaction:

As shown, the formation of vacancies on K lattice sites (V_{aK}) in $KInSe_2$ could have accompanied the evaporative loss of K. In this way, the observed K loss could cause the $KInSe_2$ contraction observed at high temperature, as well as the $KInSe_2$ consumption and $K_2In_{12}Se_{19}$ formation.

Continuous peak shifts to smaller 2θ (larger d-spacing) were also found at 500-600°C in Fig. 5, 6 (a), and 6 (b). These were likely attributable to phase transitions. There were many candidate compounds: In_4Se_3 , $InSe$, In_6Se_7 , In_9Se_{11} , In_5Se_7 , 4 polymorphs of In_2Se_3 [71], $K_2In_{12}Se_{19}$ [60], the Se analog of KIn_5S_8 (if it exists) [72], KIn_3Se_5 [70], $KInSe_2$ [61, 63, 70], $K_4In_2Se_5$ [70], $K_{12}In_2Se_9$ [73], K_9InSe_7 [73], K_2Se , K_2Se_2 , K_2Se_4 , K_2Se_5 , and K_2Se_6 [67, 68]. The structures of KIn_3Se_5 , $K_4In_2Se_5$, K_2Se_2 , K_2Se_4 , K_2Se_5 , and K_2Se_6 have not been published. Phase diagrams and structural information for the K-In-Se system could help decipher these high temperature peak shifts.

Growth temperature and annealing established different K chemical potentials, but yielded similar results, so the role of substrate Na and temperature may be separate from K chemical potential. Equilibration experiments could assist in determining the specific role of K chemical potential on phase equilibrium in the Cu-K-In-Se system, as well as any thermodynamic component to the extent of reaction (1). While chemical reactions have been shown to occur during KF PDTs [1, 5-7, 9, 10, 12-14, 29, 30, 34-38, 40, 41, 45], the specific reactants, products, extents and desirability of the reactions are relatively uncertain. The present work has outlined the stability of $CuInSe_2 + KInSe_2$ (relative to CKIS) for various conditions, and contributes to understanding the material chemistry behind the PV performance enhancements/detriments of KF PDTs, guiding more robust process engineering for K introduction, and identifying probable reactants and products in long-term degradation studies.

4. Conclusions

The effect of temperature on phase formation in the Cu-K-In-Se material system was studied. Increased substrate Na composition was previously shown to drive CKIS alloy formation (relative to $\text{CuInSe}_2 + \text{KInSe}_2$ mixed phases) during co-evaporation [35]. For Na-rich SLG substrates, changing growth temperature from 600°C to 500°C also drove the formation of CKIS alloys, as evidenced by SEM, XRD, and UV-visible spectroscopy. Na-poor Mo substrates clearly exhibited the same effect on changing growth temperature from 500°C to 400°C. CKIS alloy formation was therefore favored, relative to $\text{CuInSe}_2 + \text{KInSe}_2$, at increased substrate Na and decreased temperature. Films had resistivities, minority carrier lifetimes, and carrier concentrations in line with previous reports [35, 52, 53]. Films grown at 400°C and 500°C were annealed to 600°C, and showed K loss in proportion to initial film K content (XRF and SIMS). Annealing established increased temperature and decreased K chemical potential, while also reversing reaction (1) and advancing reaction (2) forward (by SEM, XRD, UV-visible spectroscopy, and HTXRD). Annealing's effect on reaction (1) was in excellent agreement with increased growth temperature results, despite the differences in K chemical potential for the 2 experiments—evidence that K chemical potential was *not* the mechanism by which temperature and substrate Na affected CKIS alloy formation, although phase diagram studies would be needed to affirm or refute this inference. The KInSe_2 lattice exhibited contraction at high temperature that progressed with temperature and time, as well as just time. This could have been a result of Va_K formation, driven by K evaporation (e.g. reaction (3)). However, other unexplained HTXRD peak shifts were observed at high temperature, and more structural and phase equilibrium data for K-In-Se will be needed to better understand these transitions. The present study has identified promising strategies for understanding and ultimately engineering K

bonding in CIGS to maximize initial and long-term PV performance: **Process conditions were used to establish relative CuInSe_2 , CKIS , KInSe_2 , and $\text{K}_2\text{In}_{12}\text{Se}_{19}$ phase amounts. The growth trends may prove useful for predicting the presence or absence of minor phase impurities below typical detection limits—impurities that could dominate PV-relevant electronic properties.** Furthermore, the results lay a foundation for identifying the thermodynamic and/or kinetic mechanisms ultimately controlling the formation of each Cu-K-In-Se phase, as well as predicting probable degradation routes in reliability studies.

Acknowledgement

The authors thank Stephen Glynn for a key suggestion, Kannan Ramanathan for leadership, Lorelle Mansfield, Carolyn Beall, Karen Bowers, and Stephen Glynn for assistance with experiments, Clay DeHart for contact deposition, Matt Young for SIMS, and Bobby To for SEM. EDS and HTXRD were performed at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory. The work was supported by the U.S. Department of Energy under contract DE-AC36-08GO28308.

References

- [1] A. Chirilă, P. Reinhard, F. Pianezzi, P. Bloesch, A.R. Uhl, C. Fella, L. Kranz, D. Keller, C. Gretener, H. Hagendorfer, D. Jaeger, R. Erni, S. Nishiwaki, S. Buecheler, A.N. Tiwari, Potassium-induced surface modification of Cu(In,Ga)Se₂ thin films for high-efficiency solar cells, *Nat Mater* 12 (2013) 1107-1111.
- [2] T.M. Friedlmeier, P. Jackson, A. Bauer, D. Hariskos, O. Kiowski, R. Wuerz, M. Powalla, Improved Photocurrent in Cu(In,Ga)Se₂ Solar Cells: From 20.8% to 21.7% Efficiency with CdS Buffer and 21.0% Cd-Free, *IEEE J. Photovolt.* 5 (2015) 1487-1491.
- [3] P. Jackson, D. Hariskos, R. Wuerz, O. Kiowski, A. Bauer, T.M. Friedlmeier, M. Powalla, Properties of Cu(In,Ga)Se₂ solar cells with new record efficiencies up to 21.7%, *Phys. Status Solidi RRL* 9 (2015) 28-31.
- [4] P. Jackson, D. Hariskos, R. Wuerz, W. Wischmann, M. Powalla, Compositional investigation of potassium doped Cu(In,Ga)Se₂ solar cells with efficiencies up to 20.8%, *Phys. Status Solidi RRL* 8 (2014) 219-222.
- [5] A. Laemmle, R. Wuerz, M. Powalla, Efficiency enhancement of Cu(In,Ga)Se₂ thin-film solar cells by a post-deposition treatment with potassium fluoride, *Phys. Status Solidi RRL* 7 (2013) 631-634.
- [6] L.M. Mansfield, R. Noufi, C.P. Muzzillo, C. DeHart, K. Bowers, B. To, J.W. Pankow, R.C. Reedy, K. Ramanathan, Enhanced performance in Cu(In,Ga)Se₂ solar cells fabricated by the two-step selenization process with a potassium fluoride postdeposition treatment, *IEEE J. Photovolt.* 4 (2014) 1650-1654.
- [7] F. Pianezzi, P. Reinhard, A. Chirilă, B. Bissig, S. Nishiwaki, S. Buecheler, A.N. Tiwari, 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.* 16 (2014) 8843-8851.
- [8] F. Pianezzi, P. Reinhard, A. Chirilă, S. Nishiwaki, B. Bissig, S. Buecheler, A.N. Tiwari, Defect formation in Cu(In,Ga)Se₂ thin films due to the presence of potassium during growth by low temperature co-evaporation process, *J. Appl. Phys.* 114 (2013) 194508-194508.
- [9] P. Reinhard, B. Bissig, F. Pianezzi, E. Avancini, H. Hagendorfer, D. Keller, P. Fuchs, M. Döbeli, C. Vigo, P. Crivelli, S. Nishiwaki, S. Buecheler, A.N. Tiwari, Features of KF and NaF Postdeposition Treatments of Cu(In,Ga)Se₂ Absorbers for High Efficiency Thin Film Solar Cells, *Chem. Mater.* 27 (2015) 5755-5764.
- [10] J.M. Raguse, C.P. Muzzillo, J.R. Sites, L. Mansfield, Effects of Sodium and Potassium on the Photovoltaic Performance of CIGS Solar Cells, *IEEE J. Photovolt.* 7 (2017) 303-306.
- [11] R. Kamada, T. Yagioka, S. Adachi, A. Handa, K.F. Tai, T. Kato, H. Sugimoto, New world record Cu(In,Ga)(Se,S)₂ thin film solar cell efficiency beyond 22%, in: *IEEE Photovolt. Specialists Conf.*, Portland, OR, 2016, pp. 1287-1291.
- [12] O. Lundberg, E. Wallin, V. Gusak, S. Södergren, S. Chen, S. Lotfi, F. Chalvet, U. Malm, N. Kaihovirta, P. Mende, G. Jaschke, P. Kratzert, J. Joel, M. Skupinski, P. Lindberg, T. Jarmar, J. Lundberg, J. Mathiasson, L. Stolt, Improved CIGS Modules by KF Post Deposition Treatment and Reduced Cell-to-Module Losses, in: *IEEE Photovolt. Specialists Conf.*, Portland, OR, 2016, pp. 1-4.

- [13] T. Lepetit, Influence of KF post deposition treatment on the polycrystalline Cu(In,Ga)Se₂/CdS heterojunction formation for photovoltaic application, in: Mater. Sci., Université de Nantes, Nantes, FR, 2015, pp. 132.
- [14] I. Khatri, H. Fukai, H. Yamaguchi, M. Sugiyama, T. Nakada, Effect of potassium fluoride post-deposition treatment on Cu(In,Ga)Se₂ thin films and solar cells fabricated onto sodalime glass substrates, Sol. Energy Mater. Sol. Cells 155 (2016) 280-287.
- [15] A. Laemmle, R. Wuerz, M. Powalla, Investigation of the effect of potassium on Cu(In,Ga)Se₂ layers and solar cells, Thin Solid Films 582 (2015) 27-30.
- [16] T. Kato, Cu(In,Ga)(Se,S)₂ solar cell research in Solar Frontier: Progress and current status, Jpn. J. Appl. Phys. 56 (2017) 04CA02.
- [17] C.-H. Hsu, W.-H. Ho, S.-Y. Wei, C.-H. Lai, Over 14% Efficiency of Directly Sputtered Cu(In,Ga)Se₂ Absorbers without Postselenization by Post-Treatment of Alkali Metals, Adv. Energy Mat. in press (2017) 1602571.
- [18] S.A. Jensen, S. Glynn, A. Kanevce, P. Dippo, J.V. Li, D.H. Levi, D. Kuciauskas, Beneficial effect of post-deposition treatment in high-efficiency Cu(In,Ga)Se₂ solar cells through reduced potential fluctuations, J. Appl. Phys. 120 (2016) 063106-063107.
- [19] I. Khatri, M. Sugiyama, T. Nakada, Effects of combined additional indium deposition and potassium fluoride post-deposition treatments on Cu(In,Ga)Se₂ thin film solar cells, Prog. Photovoltaics 10.1002/pip.2892 (2017) in press.
- [20] J.A. Aguiar, A. Stokes, C.-S. Jiang, T. Aoki, P.G. Kotula, M.K. Patel, B. Gorman, M. Al-Jassim, Revealing Surface Modifications of Potassium-Fluoride-Treated Cu(In,Ga)Se₂: A Study of Material Structure, Chemistry, and Photovoltaic Performance, Adv. Mater. Interfaces 3 (2016) 1600013.
- [21] E. Handick, P. Reinhard, R.G. Wilks, F. Pianezzi, T. Kunze, D. Kreikemeyer-Lorenzo, L. Weinhardt, M. Blum, W. Yang, M. Gorgoi, E. Ikenaga, D. Gerlach, S. Ueda, Y. Yamashita, T. Chikyow, C. Heske, S. Buecheler, A.N. Tiwari, M. Bär, Formation of a K-In-Se surface species by NaF/KF post-deposition treatment of Cu(In,Ga)Se₂ thin-film solar cell absorbers, ACS Appl. Mater. Interfaces 9 (2017) 3581-3589.
- [22] S. Karki, P.K. Paul, G. Rajan, T. Ashrafee, K. Aryal, P. Pradhan, R.W. Collins, A. Rockett, T.J. Grassman, S.A. Ringel, A.R. Arehart, S. Marsillac, In Situ and Ex Situ Investigations of KF Postdeposition Treatment Effects on CIGS Solar Cells, IEEE J. Photovolt. 7 (2017) 665-669.
- [23] S. Zahedi-Azad, R. Scheer, Quenching interface recombination in wide bandgap Cu(In,Ga)Se₂ by potassium treatment, Phys. Status Solidi C in press (2017) 1600203.
- [24] M. Mezher, Novel pathways to high-efficiency chalcopyrite photovoltaic devices: A spectroscopic investigation of alternative buffer layers and alkali-treated absorbers, in: Department of Chemistry and Biochemistry, University of Nevada, Las Vegas, Las Vegas, NV, 2016, pp. 164.
- [25] D. Shin, J. Kim, T. Gershon, R. Mankad, M. Hopstaken, S. Guha, B.T. Ahn, B. Shin, Effects of the incorporation of alkali elements on Cu(In,Ga)Se₂ thin film solar cells, Sol. Energy Mater. Sol. Cells 157 (2016) 695-702.
- [26] NREL, Best Research-Cell Efficiencies, in, NCPV, Golden, CO, 2016.
- [27] Press-release, ZSW Sets New World Record for Thin-Film Solar Cells, in, Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Stuttgart, DE, 2016.
- [28] D. Hariskos, P. Jackson, W. Hempel, S. Paetel, S. Spiering, R. Menner, W. Wischmann, M. Powalla, Method for a high-rate solution deposition of Zn(O,S) buffer layer for high efficiency

- Cu(In,Ga)Se₂-based solar cells, in: IEEE Photovolt. Specialists Conf., Portland, OR, 2016, pp. 1-6.
- [29] G.S. Jeong, E.S. Cha, S.H. Moon, B.T. Ahn, Effect of KF Treatment of Cu(In,Ga)Se₂ Thin Films on the Photovoltaic Properties of CIGS Solar Cells, *Curr. Photovolt. Res.* 3 (2015) 65-70.
- [30] Y.-S. Son, W.M. Kim, J.-K. Park, J.-h. Jeong, KF Post Deposition Treatment Process of Cu(In,Ga)Se₂ Thin Film Effect of the Na Element Present in the Solar Cell Performance, *Curr. Photovolt. Res.* 3 (2015) 130-134.
- [31] Z.-K. Yuan, S. Chen, Y. Xie, J.-S. Park, H. Xiang, X.-G. Gong, S.-H. Wei, Na-Diffusion Enhanced p-type Conductivity in Cu(In,Ga)Se₂: A New Mechanism for Efficient Doping in Semiconductors, *Adv. Energy Mat.* 6 (2016) 1601191.
- [32] M.A. Contreras, B. Egaas, P. Dippo, J. Webb, J. Granata, K. Ramanathan, S. Asher, A. Swartzlander, R. Noufi, On the role of Na and modifications to Cu(In,Ga)Se₂ absorber materials using thin-MF (M=Na, K, Cs) precursor layers, in: IEEE Photovolt. Specialists Conf., 1997, pp. 359-362.
- [33] C.S. Jiang, B. To, S. Glynn, H. Mahabaduge, T. Barnes, M.M. Al-Jassim, Recent progress in nanoelectrical characterizations of CdTe and Cu(In, Ga)Se₂, in: IEEE Photovolt. Specialists Conf., 2016, pp. 3675-3680.
- [34] S. Karki, P. Paul, G. Rajan, T. Ashrafee, K. Aryal, P. Pradhan, R.W. Collins, A.A. Rockett, T.J. Grassman, S.A. Ringel, A.R. Arehart, S. Marsillac, In-situ and Ex-situ Characterizations of CIGS Solar Cells with KF Post Deposition Treatment, in: IEEE Photovolt. Specialists Conf., Portland, OR, 2016, pp. 1-6.
- [35] C.P. Muzzillo, H.M. Tong, T.J. Anderson, The effect of Na on Cu-K-In-Se thin film growth, <https://arxiv.org/abs/1703.06365> submitted (2017).
- [36] E. Handick, P. Reinhard, R.G. Wilks, F. Pianezzi, R. Félix, M. Gorgoi, T. Kunze, S. Buecheler, A.N. Tiwari, M. Bär, NaF/KF Post-Deposition Treatments and their Influence on the Structure of Cu(In,Ga)Se₂ Absorber Surfaces, in: IEEE Photovolt. Specialists Conf., Portland, OR, 2016, pp. 1-5.
- [37] T. Lepetit, S. Harel, L. Arzel, G. Ouvrard, N. Barreau, Co-evaporated KInSe₂: a fast alternative to KF post-deposition treatment in high efficiency Cu(In,Ga)Se₂ thin film solar cells, in: IEEE Photovolt. Specialists Conf., Portland, OR, 2016, pp. 1-4.
- [38] E. Handick, P. Reinhard, J.-H. Alsmeier, L. Köhler, F. Pianezzi, S. Krause, M. Gorgoi, E. Ikenaga, N. Koch, R.G. Wilks, S. Buecheler, A.N. Tiwari, M. Baer, Potassium post-deposition treatment-induced band gap widening at Cu(In,Ga)Se₂ surfaces – Reason for performance leap?, *ACS Appl. Mater. Interfaces* 7 (2015) 27414-27420.
- [39] H. Elanzeery, F. Babbe, M. Melchiorre, A. Zelenina, S. Siebentritt, Potassium Fluoride Ex Situ Treatment on Both Cu-Rich and Cu-Poor CuInSe₂ Thin Film Solar Cells, *IEEE J. Photovolt.* 7 (2017) 684-689.
- [40] B. Umsur, W. Calvet, A. Steigert, I. Lauermann, M. Gorgoi, K. Prietzel, D. Greiner, C.A. Kaufmann, T. Unold, M. Lux-Steiner, Investigation of the potassium fluoride post deposition treatment on the CIGSe/CdS interface using hard x-ray photoemission spectroscopy - a comparative study, *Phys. Chem. Chem. Phys.* 18 (2016) 14129-14138.
- [41] P. Pistor, D. Greiner, C.A. Kaufmann, S. Brunken, M. Gorgoi, A. Steigert, W. Calvet, I. Lauermann, R. Klenk, T. Unold, M.-C. Lux-Steiner, Experimental indication for band gap widening of chalcopyrite solar cell absorbers after potassium fluoride treatment, *Appl. Phys. Lett.* 105 (2014) 063901-063904.

- [42] T. Maeda, A. Kawabata, T. Wada, First-principles study on alkali-metal effect of Li, Na, and K in CuInSe₂ and CuGaSe₂, Jpn. J. Appl. Phys. 54 (2015) 08KC20.
- [43] T.M. Friedlmeier, P. Jackson, D. Kreikemeyer-Lorenzo, D. Hauschild, O. Kiowski, D. Hariskos, L. Weinhardt, C. Heske, M. Powalla, A Closer Look at Initial CdS Growth on High-Efficiency Cu(In,Ga)Se₂ Absorbers Using Surface-Sensitive Methods, in: IEEE Photovolt. Specialists Conf., Portland, OR, 2016, pp. 1-5.
- [44] T. Lepetit, S. Harel, L. Arzel, G. Ouvrard, N. Barreau, Coevaporated KInSe₂: A Fast Alternative to KF Postdeposition Treatment in High-Efficiency Cu(In,Ga)Se₂ Thin Film Solar Cells, IEEE J. Photovolt. PP (2016) 1-5.
- [45] P. Reinhard, B. Bissig, F. Pianezzi, H. Hagendorfer, G. Sozzi, R. Menozzi, C. Gretener, S. Nishiwaki, S. Buecheler, A.N. Tiwari, Alkali-Templated Surface Nanopatterning of Chalcogenide Thin Films: A Novel Approach Toward Solar Cells with Enhanced Efficiency, Nano Lett. 15 (2015) 3334-3340.
- [46] Y. Zhang, R.E. Bartolo, S.J. Kwon, M. Dagenais, High Short-Circuit Current Density in CIS Solar Cells by a Simple Two-Step Selenization Process With a KF Postdeposition Treatment, IEEE J. Photovolt. 7 (2016) 676-683.
- [47] R. Wuerz, A. Eicke, F. Kessler, S. Paetel, S. Efimenko, C. Schlegel, CIGS thin-film solar cells and modules on enamelled steel substrates, Sol. Energy Mater. Sol. Cells 100 (2012) 132-137.
- [48] D. Colombara, U. Berner, A. Ciccioli, J.C. Malaquias, T. Bertram, A. Crossay, M. Schöneich, H.J. Meadows, D. Regesch, S. Delsante, G. Gigli, N. Valle, J. Guillot, B. El Adib, P. Grysan, P.J. Dale, Deliberate and Accidental Gas-Phase Alkali Doping of Chalcogenide Semiconductors: Cu(In,Ga)Se₂, Sci. Rep. 7 (2017) 43266.
- [49] N. Barreau, P. Zabierowski, L. Arzel, M. Igalson, K. Macielak, A. Urbaniak, T. Lepetit, T. Painchaud, A. Dönmez, J. Kessler, Influence of post-deposition selenium supply on Cu(In,Ga)Se₂-based solar cell properties, Thin Solid Films 582 (2015) 43-46.
- [50] Y.M. Shin, C.S. Lee, D.H. Shin, H.S. Kwon, B.G. Park, B.T. Ahn, Surface modification of CIGS film by annealing and its effect on the band structure and photovoltaic properties of CIGS solar cells, Curr. Appl Phys. 15 (2015) 18-24.
- [51] M. Theelen, V. Hans, N. Barreau, H. Steijvers, Z. Vroon, M. Zeman, The impact of alkali elements on the degradation of CIGS solar cells, Prog. Photovoltaics 23 (2015) 537-545.
- [52] C.P. Muzzillo, Chalcopyrites for Solar Cells: Chemical Vapor Deposition, Selenization, and Alloying, in: Chemical Engineering, University of Florida, Gainesville, FL, 2015, pp. 458.
- [53] C.P. Muzzillo, L.M. Mansfield, K. Ramanathan, T.J. Anderson, Properties of Cu_{1-x}K_xInSe₂ alloys, J. Mat. Sci. 51 (2016) 6812-6823.
- [54] C.P. Muzzillo, J.V. Li, L.M. Mansfield, K. Ramanathan, T.J. Anderson, Surface and bulk effects of K in highly efficient Cu_{1-x}K_xInSe₂ solar cells, <https://arxiv.org/abs/1704.01560> submitted (2017).
- [55] C.P. Muzzillo, T.J. Anderson, Surface and bulk effects of K in Cu_{1-x}K_xIn_{1-y}Ga_ySe₂ solar cells, <https://arxiv.org/abs/1704.01593> submitted (2017).
- [56] C.P. Muzzillo, L.M. Mansfield, C. Dehart, K. Bowers, R.C. Reedy, B. To, R. Noufi, K. Ramanathan, T.J. Anderson, The effect of Ga content on the selenization of co-evaporated CuGa/In films and their photovoltaic performance, in: IEEE Photovolt. Specialists Conf., Denver, CO, 2014, pp. 1649-1654.

- [57] C.P. Muzzillo, L.M. Mansfield, C. DeHart, K. Bowers, R.C. Reedy, B. To, K. Ramanathan, T.J. Anderson, Differences between CuGa/In and Cu/Ga/In films for selenization, in: IEEE Photovolt. Specialists Conf., New Orleans, LA, 2015, pp. 1-6.
- [58] S. Ishizuka, A. Yamada, M.M. Islam, H. Shibata, P. Fons, T. Sakurai, K. Akimoto, S. Niki, Na-induced variations in the structural, optical, and electrical properties of Cu(In,Ga)Se₂ thin films, J. Appl. Phys. 106 (2009) 034908-034906.
- [59] O. Lundberg, J. Lu, A. Rockett, M. Edoff, L. Stolt, Diffusion of indium and gallium in Cu(In,Ga)Se₂ thin film solar cells, J. Phys. Chem. Solids 64 (2003) 1499-1504.
- [60] M. Schlosser, C. Reiner, H.-J. Deiseroth, L. Kienle, K₂In₁₂Se₁₉, a Complex New Structure Type Based on Icosahedral Units of Se²⁻, Eur. J. Inorg. Chem. 2001 (2001) 2241-2247.
- [61] P. Wang, X.-Y. Huang, Y.-L. Liu, Y.-G. Wei, J. Li, H.-Y. Guo, Solid state synthesis at intermediate temperature and structural characterization of KInSe₂, Acta Chim. Sinica 58 (2000) 1005-1008.
- [62] I.L. Repins, B. Egaas, L.M. Mansfield, M.A. Contreras, C.P. Muzzillo, C. Beall, S. Glynn, J. Carapella, D. Kuciauskas, Fiber-fed time-resolved photoluminescence for reduced process feedback time on thin-film photovoltaics, Rev. Sci. Instrum. 86 (2015) 013907-013907.
- [63] H.-W. Ma, Guo, M.-S. Wang, GuoZhou, S.-H. Lin, Z.-C. Dong, J.-S. Huang, K₂MM'₃Se₆ (M = Cu, Ag; M' = Ga, In), A New Series of Metal Chalcogenides with Chain-Sublayer-Chain Slabs: $\infty^1[M'Se_4]-\infty^2[(MSe_4)(M'Se_4)]-\infty^1[M'Se_4]$, Inorg. Chem. 42 (2003) 1366-1370.
- [64] G.-H. Wang, H.-Y. Guo, Solid-state synthesis of K₂CuIn₃Se₆ and its crystal structure and characterization, Journal of Beijing University of Chemical Technology 31 (2004) 73-77.
- [65] J.W. Orton, M.J. Powell, The Hall effect in polycrystalline and powdered semiconductors, Rep. Prog. Phys. 43 (1980) 1263-1307.
- [66] L. Kienle, A. Simon, Microdomains and Diffuse Scattering in K₂In₁₂Se₁₉, J. Solid State Chem. 161 (2001) 385-395.
- [67] W. Klemm, H. Sodomann, P. Langmesser, Beiträge Zur Kenntnis der Alkalimetallchalkogenide, Z. Anorg. Allg. Chem. 241 (1939) 281-304.
- [68] J. Sangster, A.D. Pelton, The K-Se (Potassium-Selenium) System, J. Phase Equilib. 18 (1997) 177-180.
- [69] C.P. Muzzillo, J.D. Poplawsky, H.M. Tong, T.J. Anderson, Characterization of K in grain interiors, grain boundaries, and at the buffer interface in highly efficient Cu_{1-x}K_xInSe₂ solar cells, submitted (2017).
- [70] Z.Z. Kish, V.B. Lazarev, E.Y. Peresh, E.E. Semrad, Compounds in In₂Se₃-K₂Se, Neorg. Mater. 24 (1988) 1602-1605.
- [71] J.-B. Li, M.-C. Record, J.-C. Tedenac, A thermodynamic assessment of the In-Se system, Z. Metallk. 94 (2003) 381-389.
- [72] H.J. Deiseroth, Splitpositionen für Alkalimetallkationen in den Thioindaten MIn₅S₈ (M = K, Rb, Cs)?, Z. Kristallogr. Cryst. Mater. 177 (1986) 307-314.
- [73] J. Heine, S. Dehnen, Synthesis and Characterization of the First Salts of the ortho-Selenidoindate Anion [InSe₄]⁵⁻, Z. Anorg. Allg. Chem. 634 (2008) 2303-2308.