



Surface and bulk effects of K in highly efficient $\text{Cu}_{1-x}\text{K}_x\text{InSe}_2$ solar cells

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ARTICLE INFO

Keywords:

Cu(In,
Ga)Se₂
CIGS
Chalcopyrite
Potassium
Efficient
Alloy

ABSTRACT

To advance knowledge of the beneficial effects of K in Cu(In,Ga)(Se,S)₂ (CIGS) photovoltaic (PV) absorbers, recent Cu-K-In-Se phase growth studies have been extended to PV performance. First, the effect of distributing K throughout bulk $\text{Cu}_{1-x}\text{K}_x\text{InSe}_2$ absorbers at low K/(K+Cu) compositions ($0 \leq x \leq 0.30$) was studied. Efficiency, open-circuit voltage (V_{OC}), and fill factor (FF) were greatly enhanced for $x \sim 0.07$, resulting in an officially-measured 15.0%-efficient solar cell, matching the world record CuInSe_2 efficiency. The improvements were a result of reduced interface and bulk recombination, relative to CuInSe_2 ($x \sim 0$). However, higher x compositions had reduced efficiency, short-circuit current density (J_{SC}), and FF due to greatly increased interface recombination, relative to the $x \sim 0$ baseline. Next, the effect of confining K at the absorber/buffer interface at high K/(K+Cu) compositions ($0.30 \leq x \leq 0.92$) was researched. Previous work showed that these surface layer growth conditions produced CuInSe_2 with a large phase fraction of KInSe_2 . After optimization (75 nm surface layer with $x \sim 0.41$), these KInSe_2 surface samples exhibited increased efficiency (officially 14.9%), V_{OC} , and FF as a result of decreased interface recombination. The KInSe_2 surfaces had features similar to previous reports for KF post-deposition treatments (PDTs) used in world record CIGS solar cells—taken as indirect evidence that KInSe_2 can form during these PDTs. Both the bulk and surface growth processes greatly reduced interface recombination. However, the KInSe_2 surface had higher K levels near the surface, greater lifetimes, and increased inversion near the buffer interface, relative to the champion bulk $\text{Cu}_{1-x}\text{K}_x\text{InSe}_2$ absorber. These characteristics demonstrate that K may benefit PV performance by different mechanisms at the surface and in the absorber bulk.

1. Introduction

Recent reports have detailed power conversion efficiency enhancements when potassium fluoride and selenium were co-evaporated onto Cu(In,Ga)(Se,S)₂ (CIGS) absorbers at around 350 °C (KF post-deposition treatment (PDT)) [1–20]. RbF has also been used [3,17,18]. In particular, 7 of the last 9 world record CIGS efficiencies have employed a KF (or RbF) PDT [1,3,4,12,17,21,22], ultimately advancing the record efficiency from 20.3% to 22.9% in ~5 yr. KF PDT successes in the laboratory have now been extended to commercially-relevant chalco-genized CIGS absorbers [12], full size (0.75 m²) modules [13], and Cd-free Zn(O,S) buffers [2,12,23]. The promise of these results has spurred many investigations into K and Rb effects on CIGS, which deviate substantially from Na effects [24]. In particular, evidence has mounted that KF PDTs form a chemically modified surface layer [1], although its particular composition [1,10,25], band gap [26,27], and benefits or detriments [25,27,28] depend on the experimental techniques

employed (due in part to air sensitivity [24]). On the other hand, KF PDTs also modify grain boundaries [29] and grain interiors [19,30]. To help experimentally isolate buffer interface and bulk absorber effects, the KF PDT has been abandoned in the present work. Instead, KF co-evaporation conditions [30,31] were established that led to KInSe_2 surface layers, and separately, chalcopyrite K-incorporation throughout the bulk absorber ($\text{Cu}_{1-x}\text{K}_x\text{InSe}_2$ (CKIS))—where both of these achieved high performance. Here, the use of established KF co-evaporation conditions has helped distinguish surface and bulk effects of K, and diminished the need for ad hoc characterization of KF PDT-modified material, as the latter has led to some of the aforementioned complex and even contradictory results.

2. Experimental

Most research on chalcopyrites utilizes the three-stage co-evaporation deposition process to achieve high efficiencies at Ga/(Ga+In)

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compositions of 0.20–0.30 [1]. Here, Ga was foregone so that observations could not be attributed to Ga/(Ga + In) changes. The three-stage process was also avoided so that observations could not be attributed to altered cation profiles (potassium can affect cation diffusion [6,32]). The deposition of ~2.5 μm CKIS absorbers with x of 0–0.30 was performed at 500 °C on Mo-coated soda-lime glass (SLG/Mo) substrates, as previously described [31]. KF evaporation rates below 0.7 Å/s were used to enhance control and reproducibility of the deposition process, as previously reported [31]. For KInSe₂ surface samples, the KF rate was ramped up and the Cu rate was ramped down over a period of 1–3 min near the end of the growth. This was followed by constant rate evaporation for 0.4–3.7 min, establishing surfaces with x of 0.30–0.92. Profilometry on the final film was used to infer individual layer thicknesses from in situ molar flux data, assuming constant density. The thicknesses of the compositionally-graded intermediate layers were varied from 47 to 201 nm, while the surface layers were 26–100 nm. Among these KInSe₂ surface samples, the champion had a 132 nm intermediate layer and a 75 nm surface layer, where the surface had K/(K + Cu), or $x \sim 0.41$. A control sample with a Cu-poor surface was prepared using that same cation profile, only with no KF added. For comparison, the bulk $x \sim 0.07$, bulk $x \sim 0.22$, bulk $x \sim 0.30$, and KInSe₂ surface films had 1.5, 5.1, 7.4, and 0.4 at-% K by in situ measurement. Unlike typical KF PDT procedures [1,5,6,8–11,14–16,19,26,27,33–35], absorbers were *not* rinsed before chemical bath deposition (CBD). Time-resolved photoluminescence (TRPL) on bare absorbers was performed under low-injection conditions using a previously described system with 1.37 eV excitation and 0.92–1.31 eV detection [36]. High temperature vacuum anneals with Se over-pressure, X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), and secondary ion mass spectrometry (SIMS) were performed on bare absorbers using previously described conditions [30,31]. Bulk absorber x compositions were estimated from XRD lattice parameters [31], as CKIS alloy formation was shown to depend strongly on Na supply from the substrate [37] and temperature [30], reducing the certainty of in situ x composition measurements. Solar cells (0.42 cm²) were fabricated with 50 nm CdS, 100 nm i-ZnO, 120 nm Al:ZnO, 50 nm Ni, and 3 μm Al (grids), with photolithography isolation. Dark and 1 sun current density-voltage (JV) measurements were performed on a temperature-controlled stage at 25 °C, after calibrating the solar simulator intensity to a standard Si cell. External quantum efficiency (QE) measurements were performed with a 150 W xenon lamp focused to a 1 mm × 2.5 mm beam area chopped at 30 Hz. Room temperature capacitance-voltage (CV) measurements were performed at 10 kHz. Room temperature admittance spectroscopy (AS) revealed a single signature for every device, and activation energies were extracted from least squares fit to the data. Temperature- and illumination-dependent JV (JV(T,G)) measurements were performed at 68–302 K and 10⁻⁶ – 10⁰ suns using a neutral density filter. Electron-beam evaporation of 100–150 nm MgF₂ was applied to the best samples, and the two best devices were officially measured by the National Renewable Energy Laboratory Photovoltaic (PV) Performance Characterization Team.

3. Results and discussion

3.1. Low K/(K + Cu) throughout bulk absorber

Bulk CKIS absorbers with K/(K + Cu), or $x \sim 0$, 0.07, 0.22, and 0.30 were grown on SLG/Mo substrates at 500 °C, as shown in Fig. S1. XRD yielded smaller lattice parameters at increased x , taken as evidence of CKIS alloy formation and consistent with a previous report [31]. The formation of CKIS alloys was confirmed by vacuum annealing films to 600 °C (10 min; under Se over-pressure). After annealing, films with $x \geq 0.07$ exhibited a small but reproducible shift to larger lattice parameters that was not observed in the baseline $x \sim 0$ films, and indicated CKIS alloy decomposition (e.g. Fig. 1) [30]. Annealing therefore

showed that the non-annealed films, which were used in devices, contained CKIS alloys. The changes in PV performance with x are therefore attributed to CKIS alloying (Fig. 2), but minor KInSe₂ formation could also play a role [30,37]. A former report fabricated devices from annealed, decomposed CKIS absorbers, but the interpretation of those results was not straightforward [38]. Recent calculations have predicted relatively unfavorable formation enthalpies for CKIS alloys [39]. As previously argued [24,38], the CKIS alloys that form during Cu-KF-In-Se co-evaporation may be metastable, and future work should address connections between K_{Cu} metastability, KF PDTs, performance, and degradation rate.

The $x \sim 0.07$ film had increased open-circuit voltage (V_{OC}) and fill factor (FF), leading to higher efficiency (relative to $x \sim 0$). Further increasing x to 0.22 and 0.30 caused a reduction in short-circuit current density (J_{SC}) and FF, while V_{OC} remained constant, resulting in lower efficiency. The films with larger x sometimes delaminated from the Mo film on humid air exposure or during CBD. This was avoided with films < 1 μm in thickness [31], but solar cells were not fabricated with such thin absorbers. QE in Fig. 3 showed very similar collection for the champion $x \sim 0$ and 0.07 absorbers. Absorbers with $x \sim 0.22$ and 0.30 had decreased collection—particularly at long wavelengths, which could be a result of lower diffusion lengths (e.g. through lower lifetimes in the left part of Table 1; Fig. 4(a)). For the poor-performing $x \sim 0.22$ and 0.30 absorbers, the long wavelength QE cutoffs did not correlate with band gaps estimated from XRD. Band gaps were not estimated by growing on bare glass substrates and measuring transmittance because a previous study found that bare glass altered growth products, relative to SLG/Mo substrates [37]. The difference in apparent CdS thickness observable in Fig. 3 was incidental, and no trend in apparent CdS thickness or CdS collection was found for CKIS absorbers. The champion performance is summarized in the left part of Table 2. An anti-reflective film was applied to the $x \sim 0.07$ champion, and it was officially measured at 15.0% efficient (Fig. S2), matching the world record efficiency for a CuInSe₂-based solar cell [40]. The present study's 15.0%-efficient absorber was grown at lower temperature by ~75 °C, did not use the 'gold standard' three-stage process [40], and no attempt was made at optimizing the device stack around it, so even higher efficiencies are likely.

CV, temperature- and illumination-dependent current density-voltage JV(T,G), and AS were performed on the best devices. CV showed that $x \sim 0$, 0.07, 0.22, and 0.30 had increasing concentrations of ionized defects with increasing x (Fig. S3(a); left part of Table 1). These data agreed well with peak PL response (left part of Table 1; Fig. 4), as well as previous PL and JV measurements [31]. Therefore, the ionized defects likely corresponded to shallow acceptors, with concentrations approximately equal to hole concentrations. The depletion width at zero bias and built-in voltage of each device were extracted from CV data, and are shown in the left part of Table 1.

At low temperature, all measured devices had JV rollover when biased above V_{OC} at ~1 sun illumination (Fig. 5), which is indicative of series resistance, or a current blocking barrier near the front [41] or back [8,42–45] interface of the absorber. All K-containing samples had less severe rollover. This behavior was also reported for a KF PDT, and was taken as evidence that K reduces a back contact barrier [8]. This could also relate to the apparent resistivity decrease in CKIS with increasing x composition [30,31].

CKIS films with $x \sim 0.22$ and 0.30 exhibited rollover in the $V_{OC}(T)$ data at slightly high temperatures, relative to $x \sim 0$ and 0.07 (Fig. 6(a)). The linear $V_{OC}(T)$ data were fit over regions where the diode ideality factors were relatively constant, so activation energies for recombination with no thermally generated carriers ($V_{OC}(T = 0 \text{ K})$ in the left part of Table 2) should be a relative measure of interface and bulk recombination [46,47]. The most efficient device ($x \sim 0.07$) rolled over more strongly in $V_{OC}(G)$ at low illumination (Fig. 7(a)), which is related to relative interface, depletion region, and bulk region recombination rates [48].

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