

The effect of Na on Cu-K-In-Se thin film growth

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ABSTRACT

Co-evaporation of Cu-KF-In-Se was performed on substrates with varied Na supply. Compositions of interest for photovoltaic absorbers were studied, with ratios of $(K + Cu)/In \sim 0.85$ and $K/(K + Cu) \sim 0-0.57$. Bare soda-lime glass (SLG) substrates had the highest Na supply as measured by secondary ion mass spectrometry, while SLG/Mo and SLG/SiO₂/Mo substrates led to 3x and 3000x less Na in the growing film, respectively. Increased Na supply favored Cu_{1-x}K_xInSe₂ (CKIS) alloy formation as proven by X-ray diffraction (XRD), while decreased Na supply favored the formation of CuInSe₂ + KInSe₂ mixed-phase films. Scanning electron microscopy and energy dispersive X-ray spectroscopy revealed the KInSe₂ precipitates to be readily recognizable planar crystals. Extrinsic KF addition during film growth promoted diffusion of Na out from the various substrates and into the growing film, in agreement with previous reports. Time-resolved photoluminescence showed enhanced minority carrier lifetimes for films with moderate K compositions ($0.04 < K/(K + Cu) < 0.14$) grown on SLG/Mo. Due to the relatively high detection limit of KInSe₂ by XRD and the low magnitude of chalcopyrite lattice shift for CKIS alloys with these compositions, it is unclear if the lifetime gains were associated with CKIS alloying, minor KInSe₂ content, or both. The identified Na-K interdependency can be used to engineer alkali metal bonding in Cu(In,Ga)(Se,S)₂ absorbers to optimize both initial and long-term photovoltaic power generation.

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1. Introduction

Recent reports have detailed power conversion efficiency enhancements when potassium fluoride and selenium have been co-evaporated onto Cu(In,Ga)Se₂ (CIGS) absorbers at around 350 °C (KF post-deposition treatment (PDT)) [1–10]. Although the mechanism(s) responsible for these efficiency improvements are not fully understood, the KF PDT has been associated with multiple phenomena: *increased* hole concentration (e.g., by consuming In_{Cu} compensating donors to produce K_{Cu} neutral defects [11]) [4–7,10–13], *decreased* hole concentration (e.g., by consuming Na_{Cu}, which produces In_{Cu} compensating donors, and may also lead to an increased Mo/CIGS barrier for current flow [7]) [1,7,9], grain boundary passivation [4,14], general defect passivation [2], Cu-depleting chemical reaction(s) resulting in better near-surface inversion [1,7,9,15] or decreased valence band energy [13,16,17], morphology changes resulting in increased CdS nucleation sites [2,9], general changes in CdS growth [15], formation of a passivating K-In-Ga-Se [9,18] or K-In-Se [17] interfacial compound, and

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modified Cu-Ga-In interdiffusion [5,12]. Additional, as-yet-unsubstantiated hypotheses have also been proposed: K could reduce the surface work function [19], interfacial K-Se compounds could cause beneficial effects [14], and detrimental KInSe₂ formation could occur [5]. A PDT without KF (just Se) has also been shown to significantly alter CIGS absorbers [20,21], calling into question what 'control' absorber is appropriate for KF PDT comparison. High absorber Na and K composition has also been linked to drastically accelerated degradation in photovoltaic (PV) performance [22], which undermines the industrial 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 [22], underscoring the importance of understanding alkali metal bonding in CIGS. In a departure from work utilizing KF precursors and PDTs, recent work used Cu, KF, In, and Se co-evaporation to form Cu_{1-x}K_xInSe₂ (CKIS) alloys with $K/(K + Cu)$ composition, or x , varied from 0 to 1 [23,24]. Increasing x in CKIS was found to monotonically decrease the chalcopyrite lattice parameter, increase the band gap, and increase the apparent carrier concentration. On the other hand, moderate K compositions ($0 < x < 0.30$) exhibited significantly longer minority carrier lifetimes [23,24], relative to $x \sim 0$ and $x \geq 0.30$. That work laid a

foundation for experimentally identifying and ultimately engineering K bonding in chalcopyrite films.

While the mechanisms underlying KF PDT effects remain uncertain, it has been established that a relatively large amount of K is present at the p–n junction in the most efficient solar cells [1]. These advances have heightened interest in Cu–K–In–Se material with group I-poor (i.e. $(K + Cu)/In \sim 0.85$) and K-rich ($x > 0.30$) compositions. Processing techniques have presently been used to study the effect of Na on phase formation in Cu–K–In–Se with those compositions. Most CIGS films are grown with $Ga/(Ga + In) \sim 0.2–0.3$ and intentional gradients in cation composition [1,25,26]. However, Ga has presently 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 [5,12] and Na [27,28] have been shown to affect cation diffusion in CIGS. In order to isolate the effects of Na composition on Cu–K–In–Se growth, different substrates were used to alter the amount of Na supply during growth. Bare soda-lime glass (SLG) led to the highest Na content, while SLG/Mo and SLG/SiO₂/Mo substrates established 3x and 3000x less Na in absorbers (as measured by secondary ion mass spectrometry (SIMS)), respectively.

2. Experimental

Co-evaporation of Cu, KF, In, and Se was performed on substrates of bare SLG and SLG/Mo (“Mo”) at 500 °C, as previously detailed [24]. The $(K + Cu)/In$ composition was maintained near 0.85 for all films, while $K/(K + Cu)$ was varied between 0 and 0.58. For the suppression of Na supply, an SiO₂ diffusion barrier (~ 25 nm) was sputtered onto SLG, followed by sputtering of 200 nm Mo (“SiO₂/Mo”). Deposited film compositions were measured with X-ray fluorescence (XRF) and elemental depth profiles with SIMS. The primary SIMS ion was Cs⁺ and the analysis area had a 63 μ m diameter. ⁶³Cu⁺, ¹¹³In⁺, ³⁹K⁺, ⁹⁸Mo⁺, ⁸⁰Se⁺, and ²³Na⁺ SIMS signals for each sample were usually scaled so that the integrated ⁸⁰Se⁺ signal was 1000 counts per second. However, interference between ³⁹K⁴¹K⁺ and ⁸⁰Se⁺ occurred in the films with high K content ($x \geq 0.38$), so films’ integrated ¹¹³In⁺ signal was scaled to 44,000 counts per second. Repeated SIMS on films with $x \geq 0.38$ showed that K–Se interference was reproducibly avoided by scaling with ⁷⁶Se⁺ or ¹¹³In⁺. To compare different samples, thicknesses were also scaled using the decreased Se signal at the back interface. Symmetric X-ray diffraction (XRD) was performed with a Rigaku Ultima IV diffractometer to determine structure and assist in phase identification, as previously reported [24]. Standard diffraction patterns were calculated from published phase structures. The film morphology was observed using scanning electron microscopy (SEM), and local composition measurements were made with energy-dispersive X-ray spectroscopy (EDS) at a 13 kV accelerating voltage. The high accelerating voltage was necessary to produce enough Se K α signal for Se composition, because the sample mount was made of Al, which convoluted the Se L α (1.379 eV) and Al K α (1.486 eV) X-rays. Room temperature time-resolved photoluminescence (TRPL) was performed on bare 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 0.92–1.31 eV (details of the fiber optic system have been published elsewhere [29]). Previous work found substantial differences in TRPL response of CIGS absorbers, depending on the exact amount of air exposure [29]. This was accounted for in the present study by following the same procedure for every sample: the 3 in \times 3 in sample was removed from the vacuum system, labeled and broken into 6 pieces, and then TRPL was immediately performed on each piece. This reproducibly established 5–10 min of air exposure before TRPL for every sample, so the transients in TRPL response were minimal [29].

3. Results

First, CuInSe₂ ($x \sim 0$) was grown simultaneously on Mo and SLG substrates at 500 °C. The resulting films were very homogenous, with surfaces of triangular facets, and very similar grain size for each substrate (top, middle, and bottom of Fig. 1, respectively). When moving to Mo/CKIS with $x \sim 0.38$, substantial inhomogeneity arose (left of Fig. 2). The precipitation of large, planar crystals oriented perpendicular to the substrate caused this inhomogeneity. The precipitates appeared identical to previously observed

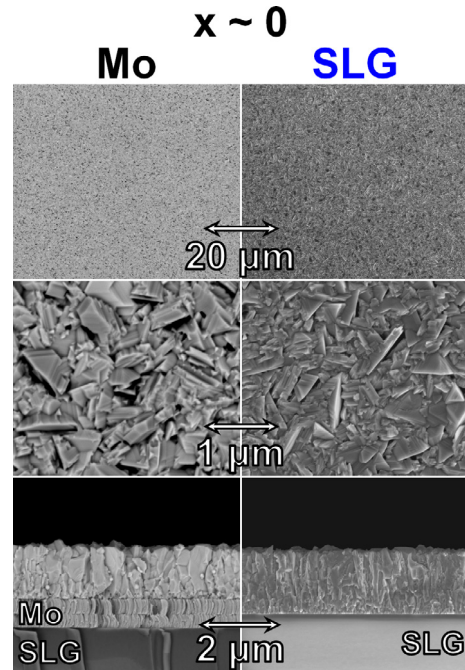


Fig. 1. Plan view (top) and cross-sectional (bottom) SEM micrographs of CuInSe₂ (CKIS with $K/(K + Cu)$, or $x \sim 0$) films on Mo (left) and SLG (right) substrates.

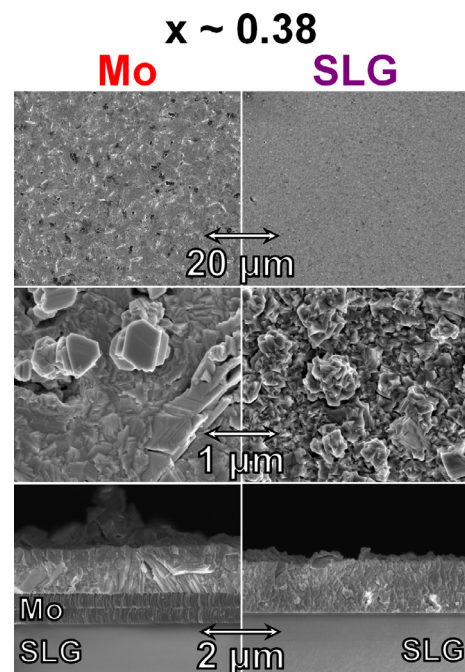


Fig. 2. Plan view (top) and cross-sectional (bottom) SEM micrographs of CKIS with $K/(K + Cu)$, or $x \sim 0.38$ films on Mo (left) and SLG (right) substrates.

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