

# A Comparative Study of the Effects of Light and Heavy Alkali-Halide Postdeposition Treatment on CuGaSe<sub>2</sub> and Cu(In,Ga)Se<sub>2</sub> Thin-Film Solar Cells

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## Abstract

The beneficial effects of alkali-metal doping in various thin-film compound photovoltaic devices such as Cu(In,Ga)Se<sub>2</sub> (CIGS), Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS), and organic-inorganic hybrid perovskite solar cells have been attracting attention as an important subject to develop photovoltaic technologies. Although systematic knowledge of alkali-metal effects is key, the detailed mechanism behind the alkali-effects in enhancing photovoltaic efficiencies has been still unclear. In the present work, the effects of light and heavy alkali-metals, namely Li and Cs, on CIGS thin-film and device properties are focused upon and comparatively studied using ternary CuGaSe<sub>2</sub> (CGS) and quaternary CIGS. It is revealed that i) the beneficial effects of heavy alkali-metal doping in ternary CGS are slight when compared to the effects obtained in quaternary CIGS, ii) CGS film surface morphology varies with CsF-Postdeposition treatment (PDT), but a variation observed with LiF-PDT is negligible and this trend is the same as the result observed from CIGS, and iii) the nominal carrier density ( $N_{cv}$ ) in both CGS and CIGS films grown on soda-lime glass substrates shows no significant increase with alkali-halide PDT regardless of the use of LiF or CsF. Nonetheless, metastable acceptor formation in CIGS is clearly enhanced with CsF-PDT in comparison to LiF-PDT. Consequently, it is suggested that the effects of elemental Li on CIGS are significantly different from the effects obtained with the other alkali-metals Na, K, Rb, and Cs.

## 1. Introduction

The effects of alkali-metal doping in Cu(In,Ga)Se<sub>2</sub> (CIGS) solar cells which enhance photovoltaic efficiencies were firstly reported in the 1990s [1]. In particular, the effects of relatively light alkali-metal Na diffused from soda-lime glass (SLG) substrates into CIGS photo-absorber layers were focused upon. Today, not only elemental Na, but also heavier elements such as K, Rb, and Cs are found to be more beneficial to obtain enhanced CIGS photovoltaic performance [2-4] and thus our interests have shifted to heavier elements such as Rb and Cs. In contrast to CIGS, the beneficial effects of light alkali-metal Li in Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) solar cells have

been reported in the literature for recent years [5]. On the other hand, the effects of light alkali-metal Li doping in CIGS have been not discussed to date. In the present work, therefore, the effects of light Li and heavy Cs alkali-halide postdeposition treatment on CIGS solar cells are comparatively studied using ternary CuGaSe<sub>2</sub> (CGS) and quaternary CIGS. Systematic knowledge of alkali-metal effects is essential and is expected to contribute to developments in compound thin-film photovoltaic technologies including chalcopyrite CIGS, kesterite CZTS, and organic-inorganic hybrid perovskite solar cells as well.

## 2. Experimental Section

The detailed CGS and CIGS film growth conditions, device fabrication procedures, and characterization methods used can be found in our previous reports [6,7]. Briefly, CGS and CIGS ([Cu]/([Ga] + [In]) ~ 0.9, [Ga]/([Ga] + [In]) ~ 0.3) films were grown by the three-stage process on alkali-free zirconia and alkali-containing SLG substrates. Postdeposition treatment (PDT) with alkali-halides LiF and CsF were performed using Knudsen cell sources at a substrate temperature of 350°C (Knudsen cell source temperatures of the LiF and CsF sources were in the range of 790-830°C and 480°C, respectively). The duration of PDT performed in this study was 10 or 20 min. The structure of solar cell devices fabricated and used for characterizations in this study was substrate (zirconia or SLG)/Mo/(CGS or CIGS)/CdS/ZnO/ZnO:Al. CGS and CIGS films and devices were characterized using scanning electron microscopy (SEM), secondary ion mass spectrometry (SIMS), capacitance-voltage ( $C-V$ ) and current-voltage ( $I-V$ ) measurements.

## 3. Results and discussion

### Ternary CGS Solar Cells

Figure 1 shows cross-sectional and surface SEM images for ternary CGS films grown using the experimental conditions of control (without PDT), LiF-PDT, and CsF-PDT. It is found from the cross-sectional SEM images that CGS films grown on alkali-free zirconia substrate possess a small grain size region in the film surface (we have observed the similar trend on alkali-free sapphire substrates as well [6]), whereas CGS films grown on SLG substrates possess a small size

grain region near the Mo back contact layer. This result is attributable to the presence of alkali-metal impurities during film growth. It is generally known that relatively heavy alkali-halide PDT leads to the formation of pores resulting in a rough surface morphology of CIGS films. Figure 1b indicates that CGS film surface became rough with CsF-PDT, similar to the case for CIGS. LiF-PDT, however, led to no significant variation in the surface morphology, implying that slight effects in the surface (CGS/CdS interface in the solar cell device structure) modification with LiF-PDT are expected.

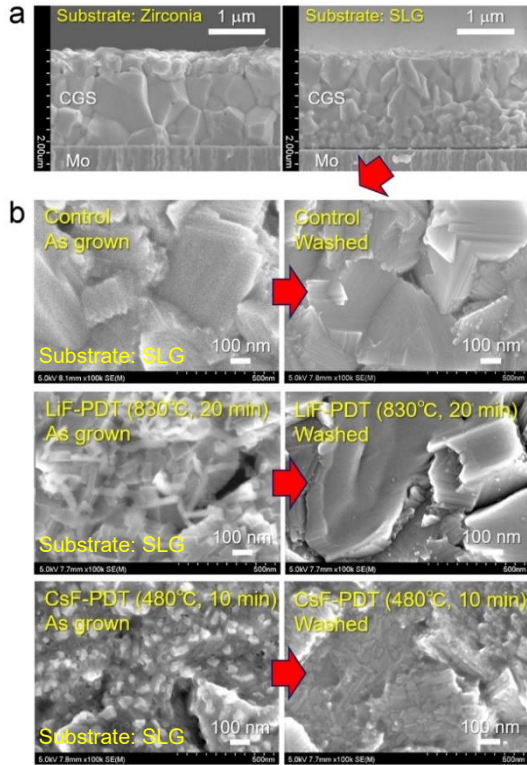


Fig. 1 (a) Cross sectional and (b) surface SEM images for as-grown and washed (in dilute ammonia solution) CGS films

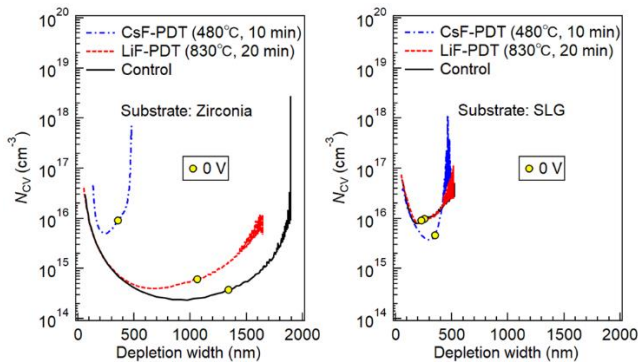


Fig. 2 Variations of  $N_{cv}$  for CGS devices fabricated on alkali-free zirconia and alkali-containing SLG substrates with and without PDT.

Figure 2 shows nominal carrier density ( $N_{cv}$ ) calculated from  $C-V$  measurement results. CsF-PDT was found to be effective in increasing hole carrier density in CGS films grown

on alkali-free substrates, whereas LiF-PDT was revealed to have very mild effects. Note that these CsF-PDT and LiF-PDT CGS films (left figure) contain alkali-metal Cs or Li of the order of  $10^{18}$ - $10^{19}$   $\text{cm}^{-3}$ . This trend was similar to the result observed from the  $N_{cv}$  variations in CIGS films [7].

#### Quaternary CIGS Solar Cells

CIGS solar cells fabricated with relatively heavy alkali-halide (such as KF and RbF) PDT are known to demonstrate enhanced photovoltaic efficiencies with the use of a thinner CdS buffer layer (conventional [without PDT]:  $\sim 50$  nm  $\rightarrow$  PDT:  $\sim 30$  nm). It was found, however, that LiF-PDT CIGS could not demonstrate enhanced efficiencies with such a thin CdS layer as shown in Fig. 3, indicating that LiF-PDT has no beneficial effects on the CIGS/CdS interface modification to enable the employment of a thinner CdS layer. Nevertheless, LiF-PDT was found to have an effect of photovoltaic performance improvements, though the effects were mild when compared to that obtained with Na or heavier alkali-metals.

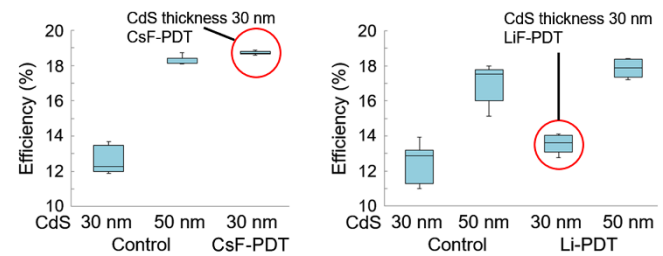


Fig. 3 Variations of photovoltaic efficiencies for CIGS solar cells grown on SLG substrates with CsF-PDT (left) and LiF-PDT (right).

#### 4. Conclusions

In this study, the effects of the lightest alkali-metal Li-doping in CGS and CIGS were comparatively studied with the effects of heavy alkali-metals. The effects of elemental Li on CGS and CIGS were found to be very unique and significantly different from the effects obtained with the other alkali-metals such as K, Rb, and Cs, and also different from relatively light alkali-metal Na.

#### Acknowledgements

The authors would like to thank Prof. P. J. Fons for fruitful discussion. This work was supported by JSPS KAKENHI Grant Number 19K05282 and also supported by a Mitsubishi Foundation Research Grant in the Natural Sciences (No. 201910001).

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