



Effect of different alkali (Li, Na, K, Rb, Cs) metals on $\text{Cu}_2\text{ZnSnSe}_4$ solar cells



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ABSTRACT

It is well established that the addition of sodium (Na) to chalcopyrite or kesterite based solar cells markedly increases the solar cell performance. In this work, we explore the effect of Na and other alkali metals like potassium (K), rubidium, caesium and lithium (Li) – on pure selenide $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) solar cells. We demonstrate the deposition of alkali metals using spin coating on e-beam evaporated metal precursors. The stack of metal precursors with alkali layer was then selenised at high temperatures to obtain a good quality CZTSe absorber. The diffusion of alkali metals into the absorber layer was confirmed using glow discharge optical emission spectroscopy. Samples doped with Na or K have shown improvement in the open circuit voltage. A maximum power conversion efficiency of 8.3% (without anti-reflection coating) and a top open circuit voltage 430 mV was achieved for combination of K and Na. Amongst the rest of alkali metals, Li looks the most promising dopant as far as optoelectronic properties are concerned.

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1. Introduction

Thin film photovoltaics are gaining prominence with record efficiencies reaching up to 22.3% for $\text{Cu}(\text{In,Ga})(\text{S}_x\text{Se}_{1-x})_2$ (hereafter referred as $\text{CIGS}_x\text{Se}_{1-x}$, $0 \leq x \leq 1$) [1]. However, the rapidly progressing display industry which uses indium and gallium will eventually limit the production of $\text{CIGS}_x\text{Se}_{1-x}$ due to the scarcity of these elements [2].

Kesterites like $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ (hereafter referred as $\text{CZTS}_x\text{Se}_{1-x}$, $0 \leq x \leq 1$) with their less toxic nature and more abundant elements are a promising alternative [2]. A record efficiency of 12.6% was demonstrated [3], however, this is still far from the theoretical Shockley-Queisser (SQ) limit of ~30% [4]. Open circuit voltage (V_{oc}) deficit continues to be a key problem with the record cell reaching only 62.6% of its SQ limit [2].

Addition of sodium (Na) to improve the performance of kesterite based cells has been inspired from the beneficial effects of Na doping in chalcopyrite based absorbers. Besides affecting the size of grains, Na also enhances the V_{oc} and fill factors of the devices, both these factors are largely sensitive to defects and traps [5–10].

Unlike $\text{CIGS}_x\text{Se}_{1-x}$, first principles calculations for $\text{CZTS}_x\text{Se}_{1-x}$ grain boundaries suggest that deep states do exist in the gap, which are expected to act as non-radiative recombination centres [11]. Gershon et al. [12] recently demonstrated diffusion of Na to internal and external surfaces of the absorber in order to passivate them [13–15]. In addition, Na showed increase in the hole concentration in monocrystalline and polycrystalline $\text{CZTS}_x\text{Se}_{1-x}$ crystals [16,17].

Potassium (K) is another alkali metal that has been incorporated into $\text{CZTS}_x\text{Se}_{1-x}$ / $\text{CIGS}_x\text{Se}_{1-x}$. In case of $\text{CZTS}_x\text{Se}_{1-x}$, presence of K suppresses the loss of tin and reduces the production of secondary phase zinc sulfide [18] resulting in lesser loss of zinc. K doping has shown to increase the crystallinity of $\text{CZTS}_x\text{Se}_{1-x}$ film and enhance the (112) preferred orientation.

In this study we aim to explore the effect of different alkali elements such as lithium (Li), sodium (Na), potassium (K), rubidium (Rb) and caesium (Cs) – on pure selenide CZTSe ($\text{CZTS}_x\text{Se}_{1-x}$, $x = 0$) solar cells. The inclusion of alkali elements was done by spin coating followed by selenisation at high temperature leading to the formation of the CZTSe absorber containing the alkali atoms. The purpose of this study is to give an overview of the impact of different alkali elements on the optoelectronic and electrical properties of CZTSe solar cells. We believe,

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Table 1

Overview of the sample set used in the study. The columns in the table highlight the differences in substrates and fabrication process used for processing of the solar cell. A front contact of Ni/Al was deposited for all the samples selenised in Annealsys furnace. No front contact was deposited for samples selenised in QRTF furnace.

Sample set	Substrates	Selenisation furnace	Concentration of alkali salts in water	Reported electrical characteristics after (A)/before (B) annealing
SLG-B	SLG-B	QRTF	LiF - 0.1 M	A
			NaF - 0.1 M	
			KF - 0.1 M	
			RbF - 0.01 M	
			CsF - 0.005 M	
		Reference		
		Annealsys	NaF - 0.1 M	A
			KF - 0.1 M	B
			NaF:KF (2:1)	A
			Reference	
Reference				
SLG	SLG	QRTF	LiF - 0.1 M	A
			RbF - 0.01 M	
			CsF - 0.005 M	
			Reference	
			Reference	
		Annealsys	Reference	

the results of this study will be helpful to initiate a detailed investigation into alkali elements that have a potential to improve the CZTSe devices.

2. Experimental details

2.1. Fabrication

A 3 mm thick soda lime glass sputtered with 500 nm molybdenum (Mo) was purchased from Guardian Industries. Two different kinds of substrates were used: I) with a 200 nm intermediate barrier layer of Silicon Oxynitride between soda lime glass and Mo to prevent in-diffusion of alkali metals (hereafter referred to as SLG-B) II) without any barrier layer (hereafter referred to as SLG).

Tin, zinc and copper were deposited on the aforementioned substrates with thickness of 215, 95 and 110 nm respectively, using Pfeiffer e-beam evaporation. Before selenisation, alkali metals were spin coated on the stack of metal precursors. Fluoride salts of alkali metals were dissolved in water with appropriate concentrations (lithium fluoride (LiF) = 0.1 M, sodium fluoride (NaF) = 0.1 M, potassium fluoride (KF) = 0.1 M, rubidium fluoride (RbF) = 0.01 M, caesium fluoride (CsF) = 0.005 M) and this was used as a solution for spin coating. The

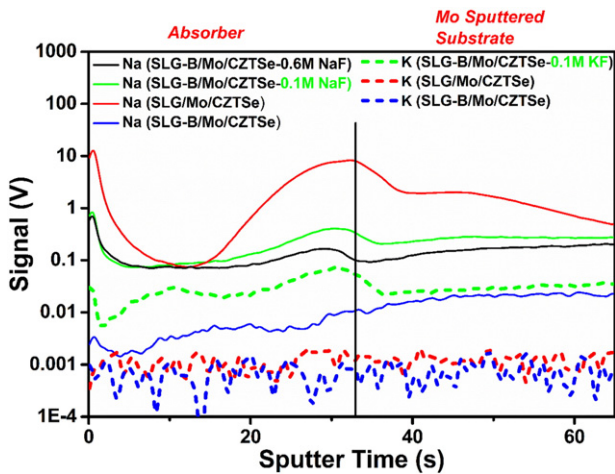


Fig. 1. GDOES measurements done on SLG-B/Mo/CZTSe, SLG/Mo/CZTSe, SLG-B/Mo/CZTSe-NaF and SLG-B/Mo/CZTSe-KF samples. Sputter time = 0 s indicates the top surface of the CZTSe absorber layer. The absorbers were synthesised in Annealsys.

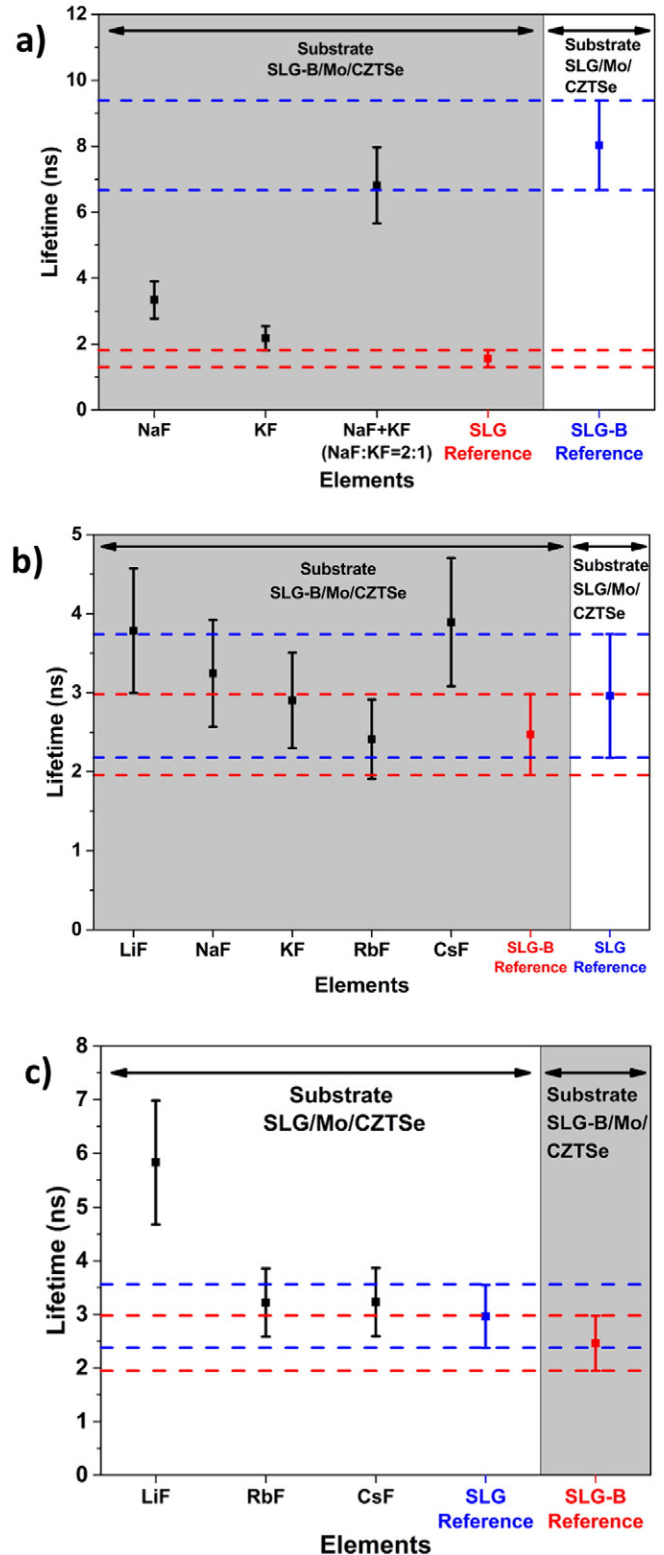


Fig. 2. Average minority carrier lifetime values obtained from TRPL measurements (a) on SLG-B/Mo/CZTSe samples selenised in Annealsys Furnace. (b) on SLG-B/Mo/CZTSe samples selenised in QRTF Furnace. (c) on SLG/Mo/CZTSe samples selenised in QRTF furnace. The x-axis indicate fluoride salts of alkali metals used for doping of absorber layers. The red and blue dotted lines indicate the standard deviation in the minority carrier lifetime of reference samples (CZTSe absorbers without any external doping of alkali metals) over different selenisation runs. The area shaded by grey colour show the minority carrier lifetime of samples selenised on SLG-B substrates. The unshaded area shows the minority carrier lifetime of samples selenised on SLG substrates.

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