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Practical limitations to selenium annealing of compound co-sputtered Cu_2ZnSnS_4 as a route to achieving sulfur-selenium graded solar cell absorbers

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Abstract

The suitability of selenium annealing as a technique to introduce energy band gap gradients via sulfur-selenium substitution in Cu_2ZnSnS_4 (CZTS) films is evaluated. Compound co-sputtered CZTS precursors are annealed in selenium atmosphere at 425°C, either as-deposited or after a short time sulfur pre-anneal. The films are investigated by Raman spectroscopy and X-ray diffractometry, and the spatial distribution of elemental species measured by secondary ion mass spectrometry and energy dispersive X-ray spectroscopy. Sulfur-selenium gradients are not achieved for the as-deposited precursor. Sulfur-selenium gradients are achieved in the early stages of annealing for pre-anneal samples, where $Cu_2ZnSn(S,Se)_4$ (CZTSSe) formation is found to be correlated spatially with sodium distribution. These gradients are lost as the annealing progresses. Selenisation occurs by CZTSSe grain growth, rather than by direct substitution of selenium for sulfur. The spatial correlation of high sodium concentration with CZTSSe formation suggests that liquid-phase sodium selenide facilitates selenium incorporation during recrystallisation, limiting the practicality of anion-grading of CZTSSe during the annealing step as a means of establishing a graded band gap.

Keywords: CZTSSe, diffusion, crystallisation, sodium, band gap gradient.

1. Introduction

The copper-zinc-tin-sulfide/selenide quaternary semiconductor material (hereafter CZTSSe or CZTS for the pure sulfide) is seen as a potential replacement for the mature copper-indium-gallium-selenide (CIGS) system as the absorber material in thin film solar cells. Although its record device sunlight-to-power efficiency remains 12.6% [1], CZTS absorbers are composed of earth-abundant materials, and show promise for future solar cell applications and as model systems for the improvement of other technologies. High efficiency CIGS solar cells employ In-Ga gradients through the thickness of the absorber film to modify the band gap and minimise recombination [2]. It is reasonable to expect the necessity of such band gap engineering in

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