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# Influence of precursor uniformity on the performance of $Cu_2ZnSnS_xSe_{4-x}$ thin film solar cells prepared by the sputtering method

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ABSTRACT

We report the effects of precursor uniformity on the efficiency of $Cu_2ZnSnS_xSe_{4-x}$ (CZTSSe) solar cells using sputtered precursors. The reduction of Sn cluster agglomeration in the Cu/Sn/Zn stacked precursor created synthesis of more uniformly distributed CZTSSe absorbers during the annealing process. The secondary phase difference between the 80 W and 40 W sputtered CZTSSe absorbers was confirmed with Raman analysis at 178 $cm^{-1}$ and 259 $cm^{-1}$. The 40 W sputtered CZTSSe cell produced blue region enhancement of external quantum efficiency results due to improvement of the pn-junction properties. The CZTSSe 40 W cells achieved a maximum power conversion efficiency of 5.7% and short-circuit current of 32.4 $mA/cm^2$.



## 1. Introduction

In past years, $Cu(In,Ga)Se_2$ (CIGS) and CdTe thin-film solar cells have attracted attention with their high power conversion efficiency (PCE) (>22%) [1,2]. However, it was difficult to acquire high market share because of the toxicity (Cd) and scarcity of some of their components (indium, gallium, and tellurium). In order to replace CIGS and CdTe thin-film solar cells, $Cu_2ZnSnS_xSe_{4-x}$ (CZTSSe)-based solar cells have been proposed as non-toxic alternatives made of materials that are abundant. CZTSSe material has been considered a promising solar energy absorption layer that has a high absorption coefficient ($10^{-4}$ $cm^{-1}$) and suitable bandgap energy (1.0–1.5 eV) [3–6]. Many fabrication techniques have been studied for use in CZTSSe solar cell manufacturing, such as solution-based processes, sputtering processes, and co-evaporation [7–9]. The most efficient fabrication method is the solution-based process reported by IBM with PCE of 12.6% CZTSSe [7], followed by sputtering with PCE of 12.3% CZTSSe [8], and co-evaporation with PCE of 11.6% $Cu_2ZnSnSe_4$ (CZTSe) [9]. However, solution-based processes using toxic hydrazine and co-evaporation are not suitable for large scale production because of very high toxicity and small deposition area. Among these methods, sputtering is the most suitable for mass production because it is non-toxic and less expensive. For these reasons, the sputtering method is now studied by many research groups for commercialization of CZTSSe solar cells.

The stoichiometry and roughness of the CZTSSe have been known to be crucial parameters of the sputtering method to achieve high PCE, and their effect on the PCEs of solar cell has been studied by many researchers [10,11]. PCE of 10.2% was achieved for a CZTSSe solar cell by optimizing the ratio of Zn/Sn, and the relationships between the Zn content, carrier density, and depletion region were also investigated [10]. Furthermore, the roughness of the $Cu_2ZnSnS_4$ absorber layer fabricated using various short-term sulfurization processes affected the efficiency of the solar cells [11]. Therefore, it is important to investigate the surface roughness to improve the PCEs of CZTSSe solar cells. We deposited precursors using different levels of sputtering power in order to form a flat surface for a CZTSSe absorber film. We then investigated the correlation between the absorber layer morphology and efficiency improvement of the CZTSSe solar cells. The solar cell fabricated with the CZTSSe film sputtered at 40 W shows the best conversion efficiency (5.7%).

## 2. Experiment

### 2.1. Metallic layers and precursor preparation

The optimization was studied regarding the sputtering power and argon pressure, which are critical parameters in the CZTSSe solar cell process. The CZTSSe thin films and metal layers were deposited on Mo-coated soda lime glass (SLG) substrates. The base pressure before Cu/

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