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Morphological control of $Cu_2ZnSn(S,Se)_4$ absorber films via inverted annealing for high-performance solar cells

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ABSTRACT

In recent years, the method of forming $Cu_2ZnSn(S,Se)_4$ (CZTSSe) by heating precursors has been widely used, but the chalcogen vapor conditions and the placement of the sample have not been disclosed completely. Here, we demonstrate a novel inverted annealing process that enables the reaction between the chalcogen vapor and precursors to remain constant. As a result, we obtained CZTSSe absorber films with an improved morphology and a uniformly distributed elemental composition. The inverted annealed samples showed less variation in the S and Se content as well as in the statistical analysis of the device performance compared with those prepared via the original annealing process. These variations in the S and Se content were confirmed several times through X-ray diffraction, energy-dispersive X-ray, and external quantum efficiency analysis. A pn-junction analysis using a Mott-Schottky plot was also conducted. We anticipate that the inverted annealing process will become widely used as it is easily applicable and effective in improving the morphology of CZTSSe absorber films.

1. Introduction

Following the invention of $Cu(In,Ga)(Se,S)_2$ (CIGS) solar cells, ones made of $Cu_2ZnSn(S,Se)_4$ (CZTSSe), in which non-toxic earth-abundant elements are used, have been extensively studied in recent decades [1–4]. In the early days of CZTSSe solar cell development, a co-evaporation method, the mainstream method for producing CIGS solar cells, was adopted to fabricate CZTSSe absorber films [5–7]. However, CZTSSe solar cells using co-evaporation have shown relatively low power conversion efficiency (PCE) and currently, most CZTSSe absorber films are obtained by forming precursors followed by heat treatment [8–12]. There are many methods for forming the precursors, such as with hydrazine, nanoparticles, electrodeposition, dimethyl sulfoxide, dimethyl formamide, and sputtering; the latter method has resulted in high performance of more than 10% PCE [13–19]. Although the method of forming CZTSSe absorber films using annealing has become mainstream, most of the details and analyses are secrets that have not been disclosed so far. In addition, although the effect of the morphology of the CZTSSe absorber films on solar cell performance has been steadily studied [20–24], there is still room for improvement.

In a previous study, we quantified the specifications of the graphite box used in the annealing process and reported the effects of this on the performance of CZTSSe solar cells [25]. In this study, we demonstrate a simple inverted annealing process using sputtered precursors. With this approach, we enabled the precursors to react more uniformly with the chalcogen vapor and improved the surface morphology of the CZTSSe absorber films. The elemental distribution and overall solar cell performance were improved according to statistical analysis of the solar cell parameters, and we achieved a PCE of up to 7.1%.

2. Experimental section

2.1. Fabrication of the precursors and CZTSSe absorber films

A Mo layer with a thickness of 1 μm was deposited as the positive electrode using DC sputtering with 280 W (10.8 W/cm^2) of power on 2 mm-thick soda-lime glass (SLG). To form the CZTSSe absorber film, Zn and Cu layers using DC sputtering and an Sn layer using RF sputtering were sequentially deposited with 50 W (1.1 W/cm^2) of power. The Ar atmospheric pressures for the Mo and precursor sputtering were

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