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Impact of sequential annealing step on the performance of $Cu_2ZnSn(S,Se)_4$ thin film solar cells

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In this study, we investigated influence of sequential heat treatment on the structural, morphological and optical properties of $Cu_2ZnSn(S,Se)_4$ (CZTSSe) thin films. Specifically, after preparation of sputtered Cu, ZnS, and Sn stacked layers, CZTSSe thin films were synthesized by sequential heat treatment (sulfurization follow by selenization). Analyses of the processed films show that non-uniform selenium distribution through the depth of the films can be obtained by introducing a controlled amount of selenium in the second heat treatment step. The top region of the film becomes selenium rich, while the bottom region is selenium poor. This structure has higher absorption coefficients than the uniform ones. In addition, the uneven composition distribution may lead to a bandgap gradient in the film, which can reduce the photocurrent loss. Finally, numerical modeling corroborates the potential of selenium gradient films for high efficiency CZTSSe solar cells.

1. Introduction

Cu_2ZnSnS_4 (CZTS) has drawn extensive research attention in recent years. CZTS is a direct bandgap semiconductor with suitable bandgap energy and a high absorption coefficient. In addition, it is characterized by earth abundant and environmentally friendly component elements which are the prerequisites for cost-efficient photovoltaic application. For these reasons, CZTS is considered as a promising absorber material of thin film solar cells (TFSC). In the past years, the reported efficiency of CZTS TFSC has increased from 0.66% [1] to 9.2% [2]. In 2013, Solar Frontier and IBM Corporation jointly reported a champion efficiency of 12.6%, achieved by alloying CZTS with selenium [3]. CZTS related solar cells with efficiency higher than 10% were also demonstrated by various research groups [4–6]. Rapid research progresses in CZTS-based solar cells benefit from the similarities in the optical and electronic properties between CZTS and $Cu(In,Ga)Se_2$ (CIGS). These similarities allow the knowledge gained from the mature CIGS technology to apply to the research of CZTS related TFSC.

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However, CZTS has unique properties that are different from CIGS, which cause particular electrical loss mechanism, such as recombination at the absorber/buffer interface and incomplete collection of photo-generated carriers [7]. The interface recombination is caused by a suboptimal conduction band alignment. It is reported that the conduction band minimum (CBM) of CZTS is about 0.1 eV higher than that of CdS [8,9]. Thus, a cliff-like conduction band alignment is formed, resulting in significant recombination at the absorber/buffer interface. On the other hand, the incomplete collection of photo-generated carriers is caused by a small carrier diffusion length. It is estimated that the summation of space-charge width and the minority carrier diffusion length is only 530 nm [10]. Therefore, incomplete collection of photo-generated carriers generated beyond 530 nm into the CZTS layer can be a significant electrical loss mechanism.

Some works have been done focusing on dealing with the above mentioned electrical losses. The interface recombination loss is suppressed by using alternative buffer layers (ZnS and In_2S_3 etc. [11–15]) to increase the CBM of buffer layer. Thus a less detrimental spike-like band alignment is formed. Collection loss is relieved by incorporation of Ge into the absorber layer. Control of the Ge compositional profiles (e.g., the Ge/Sn ratio) along the film thickness results in bandgap energy gradient of the absorber layer [16]. It is suggested that bandgap gradient is responsible for the improved solar cell performance.

Alternatively to the above mentioned strategies, control of the ratio of anion composition can also influence the bandgap. Increase of Se relative content in the CZTSSe alloy allows tuning the bandgap from 1.5 eV to 1.0 eV, with primary the CBM downshift [8]. Thus, an absorber structure with gradual decrease of Se from the surface to the back will result in suitable band alignment at the absorber/buffer interface and bandgap gradient in the absorber layer simultaneously. Despite significant potential for the bandgap grading effect, however, the bandgap grading through Se grading has not yet been explored much [17].

In this study, we analyze the viability of sequential sulfurization and selenization process steps for the synthesis of bandgap graded $Cu_2ZnSn(S,Se)_4$ (CZTSSe). The effect of the annealing parameters is investigated on precursors obtained by sputtered stacked layers. Characterization of the processed film indicates that Se content decrease towards the back contact. Device modeling suggests that electrical loss of the Se graded device is significantly reduced compared to that of uniform composition profiles. The reduced electrical loss can be attributed to the spike-like conduction alignment at the absorber/buffer interface and electric field formed by Se uneven distribution. These results corroborate the potential of sequential heat treatment for high efficiency CZTSSe solar cells.

2. Experimental detail

2.1. Preparation of CZTSSe film

ZnS/Sn/Cu stacked layers were deposited on SLG by sputtering. The conditions for the deposition of each layer were: zinc sulfide (power: 100 W, argon gas pressure: 0.6 Pa), tin (power: 60–80 W, 0.6 Pa) and copper (60–80 W, 0.6 Pa). The deposition of the stacked layers was repeated for 5 times to get desired thickness and relatively homogeneous composition distribution in the precursors. In order to study the CZTSSe formation, the samples were underwent two sequential annealing steps. In the first annealing step, the stacked layer was placed in a graphite box by introducing 500 mg sulfur powder, and then annealed in a tube furnace at 540 °C for 30 min with argon gas flow at normal pressure (sulfurization). After sulfurization, CZTS film is obtained. The prepared CZTS film was cut into pieces. Some of them underwent a second annealing step. The samples were placed in another graphite box with controlled amount of selenium powder, and then annealed in a rapid thermal process (RTP) furnace (selenization). In the selenization step, parameters (temperature, time and the mass of selenium introduced in the graphite box) were adjusted to control of selenium incorporation. Table 1 summarizes the annealing parameters for the different processed samples.

2.2. Structural characterization and properties measurement of CZTSSe

The crystal structures of the samples were characterized by an X-ray diffractometer (XRD) with Cu K_α radiation ($\lambda = 1.5418$ Å, Rigaku, Dmax 2500). Raman spectra with an excitation wavelength of 532 nm were recorded using a lab Raman system (Jobin Yvon, T64000). The morphologies and compositional distributions were investigated by scanning electron microscopy (SEM, Hitachi, S-4800) equipped with an energy dispersive X-ray spectroscopy (EDS) system (EDAX Genesis 2000). Optical properties of CZTS films were examined using an ultraviolet–visible (UV–Vis) spectrophotometer (Unico,

Table 1
Parameters for sequential step annealing.

Sample	Sulfurization			Selenization		
	Mass of S (mg)	Temperature (°C)	Time (min)	Mass of Se (mg)	Temperature (°C)	Time (min)
Se5	500	540	30	5	540	5
Se15	500	540	30	40	540	15
S30	500	540	30	–	–	–