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Original Research

One-pot hydrothermal synthesis and fabrication of kesterite $Cu_2ZnSn(S,Se)_4$ thin films

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ABSTRACT

Kesterite $Cu_2ZnSn(S,Se)_4$ (CZTSSe) powder was synthesized by a hydrothermal process. The thin films were fabricated by physical vapor deposition of CZTSSe powder followed by a thermal annealing process. The kesterite microstructure was identified by the X-ray diffraction and Raman spectroscopy. The morphology and elemental composition of CZTSSe thin films were also investigated. The dependence of resistance on the temperature of CZTSSe film was measured and the thermal activation energy of conductivity was estimated to be 0.33 eV based on Arrhenius plot of resistance versus temperature. A high absorption coefficient ($> 10^4$ cm^{-1}) of CZTSSe was found in the visible and NIR regions of the spectrum. A direct band gap structure with band gap energy of 1.46 eV was also estimated for CZTSSe films. The photoconductivity was measured under both AM 1.5G and NIR illumination and a stable and fully recoverable photoconductivity was observed for both as-deposited and annealed CZTSSe films. The annealed films show a higher photoconductivity than the as-deposited films under both AM 1.5G and NIR lights.

1. Introduction

As the increasing demand for renewable and green energy sources, various techniques, such as hydroelectricity [1], fuel cells [2] and photovoltaics (PVs) [3] have been developed as the alternative energy sources. Among different renewable energy technologies, PVs have attracted much attention due to their manufacturability, availability, usability and cost effectiveness. Among advanced PV technologies, thin film PV devices have already been largely manufactured based on CdTe as the absorber material. Although CdTe based solar cells exhibit high performance, limited supply of Te source and high toxicity of Cd would influence searching of new absorber materials in PV devices.

In order to address the above issues in CdTe-based PV devices, new materials have been investigated to replace CdTe [4–6]. One of the most promising candidates is $Cu_2ZnSn(S,Se)_4$ (CZTSSe). This material is composed of earth-abundant and non-toxic elements while it has a tunable band gap from 1.0eV to 1.5 eV [7], a direct band gap structure and a high absorption coefficient of 10^4–10^5 cm^{-1} [8]. Thus, CZTSSe is considered as a better replacement of the previously invented $Cu_2InGe(S,Se)_4$ (CIGSSe) for solar energy absorption [9]. However, compared with the current recorded efficiency (22.3%, Solar Frontier, Dec 2015) [10] of CIGS, CZTSSe-based cells could only reach 12.6% up to date [11]. Researchers also pointed out that the controllability of phase pure CSTSSe and the fabrication conditions were still the major problems from the synthesis to the fabrication of CZTSSe-based PV devices [12,13].

Since the first report by Ito et al. [14] on the synthesis and photonic properties of CZTS, various vacuum and non-vacuum approaches have been developed to synthesis this material. In vacuum approaches, sputtering of metal stacks or elemental sources were the first successful paths [15–17]. Also, fabrication of CZTS by co-evaporation was reported by Tanaka et al. [18] and further developed by other groups [19,20]. The current championed efficiency through vacuum approach is 8.4%, which was reported by IBM [21]. The vacuum approaches could produce perfect CZTS/CZTSe but it is costly. Thus, cheaper non-vacuum methods were developed. Currently the solution-based method was the most successful approach [22,23] and the 12.6% of efficiency was reported [11]. Thus, the solution-based method is now expected for a higher efficient CZTSSe cell fabrication.

However, several issues are still remained even for the solution-based synthesis methods. For example, the most commonly used solvents are oleylamine and hydrazine. Both of them are toxic and environmentally harmful chemicals and not suitable for a scalable manufacturing process, such as MW or higher power levels. Also, it is preferred to finish the synthesis in one pot rather than using the complicated preparation of metal or metal sulfide precursors. Moreover, the

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element ratio is another important variable. Chen et al. [24] suggested a Cu-poor/Zn-rich and Wang et al. [11] mentioned an element ratio of Cu/(Zn + Sn) = 0.8 and Zn/Sn = 1.1 in their successful CZTSSe-based soar cells.

In this paper, the synthesis of CZTSSe powder by a simple one-pot method is reported. The fabrication of CZTSSe films was attempted by physical vapor deposition (PVD) of synthesized powder. The objective of this research is two folds: firstly, to understand the fundamental properties of CZTSSe thin films and their controllability in the film fabrication process and secondly, to understand whether CZTSSe thin films can be fabricated by PVD method in order to incorporate this new material in advanced manufacturing technology of solar cells. We believe that the results obtained support the above objective by a greater extent.

2. Experimental details

CZTSSe powder was synthesized by a hydrothermal process. First, 0.134 M copper (II) sulfate ($CuSO_4{\cdot}5H_2O$), 0.067 M zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$) and 0.067 M tin (IV) chloride ($SnCl_4{\cdot}5H_2O$, 98%) were mixed with 150 ml of water. Then, 0.8 mol of thiourea (CH_2SNH_2) and 0.067 mol of selenium (IV) oxide (SeO_2) were added to the mixture. All chemicals were purchased from Fisher Scientific supplier. The mixture was sonicated for 15 min and transferred into an autoclave. The hydrothermal reaction was continued for 12 h at 300 °C. After the system was naturally cooled down, the precipitate was filtered and washed with ethanol for several times (> 5) and water. The cleaned black powder was dried in argon at 110 °C for 1 h. An annealing process was carried out at 550 °C in argon gas (downstream), which flows through a small amount of sulfur powder placed at 300 °C in a tube furnace for 1 h. Sulfur was added to prevent the sulfur loss during the heating process. Fig. 1 shows the experimental steps for the synthesis of CZTSSe powder and fabrication of CZTSSe films.

CZTSSe films were deposited by a PVD method on a clean glass substrate. The substrates were cleaned with acetone, 2-propanol and DI water. A small amount of synthesized powder was placed on a tungsten boat filament and evacuated the PVD system down to a pressure of 10^{-7} Torr. The filament was heated to a higher temperature for evaporation (> 1200 °C) while avoiding the separation of major compounds due to different melting points (e.g. Cu_2S: 1130 °C; ZnS: 1185 °C; SnS: 882 °C). Films were stored in a vacuum desiccator to avoid exposure to the atmosphere. The CZTSSe films were annealed in argon at 280 °C for 1.0 h. The crystal structures of both bulk and thin-film CZTSSe were studied with the X-ray diffraction (XRD) measurements using a Cu Kα radiation. Raman spectroscopy of thin film CZTSSe was collected by a Jobin Yvon Horiba Confocal Raman Spectrometer. The surface morphology and elemental composition of CZTSSe films were studied with the scanning electron microscopy (SEM, Hitachi S-4800) and energy dispersive X-ray spectroscopy (EDS, Oxford INCA). The optical transmittance spectra of CZTSSe were measured by a Perkin-Elmer, Lambda 1050 UV/VIS/NIR spectrophotometer. In order to measure the electrical properties of CZTSSe films, two Au electrodes were deposited on the surface of films by vacuum thermal evaporation through a shadow mask. Au could form a good ohmic contact on CZTSSe as mentioned by Biccari et al. [25]. The dependence of resistance on temperature was measured in a vacuum chamber in the range of 25–140 °C. The temperature of the sample was measured with a thermocouple in contact with the CZTSSe films. An electronic resistance meter (Keithley 2420 model) was connected to the vacuum chamber to measure the resistance. The photoresponse was investigated under both AM 1.5G (1 standard sun) light and NIR light emitting diode (LED) array (2.16 μW/mm^2 light intensity and wavelength of 850 nm).

The superstrate CZTSSe cell was fabricated on a FTO (fluorine doped tin oxide) glass substrate. A ZnO layer (50 nm) was deposited by magnetron sputtering method followed by a deposition of CdS layer (50 nm) by a chemical bath deposition (CBD) method. Deposition of CdS by CBD method is described elsewhere [6]. After rinsing with deionized water and air drying, the CdS films was annealed in 300 °C for 1 h in argon. The CZTSSe layer was deposited by vacuum evaporation method as described above. The solar cells were finished with coating an Au film by a vacuum thermal evaporation method directly on both as-deposited and annealed CZTSSe films. The active area of device was defined by the area of gold electrodes.

The current density-voltage (J-V) characteristics of CZTSSe solar cells were tested with a Newport solar simulator (92251A-1000) connected with a Keithley 2420 source meter. The solar simulator was equipped with an AM 1.5G solar spectrum. The incident light intensity was 100 mW/cm^2.

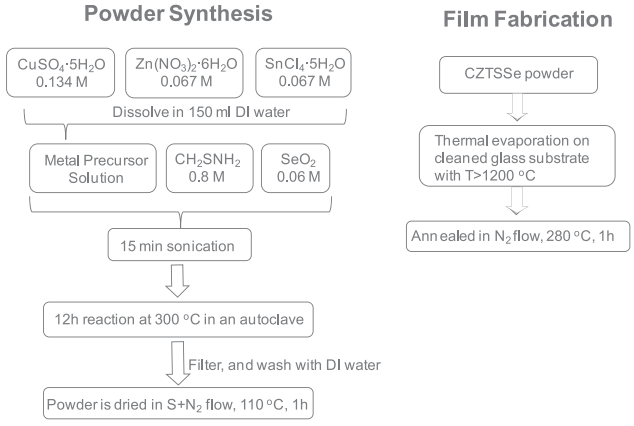

Fig. 1. Flow diagram of CXTSSe powder synthesis and film fabrication.

3. Results and discussion

Fig. 2 shows the XRD results of both CZTSSe powder and CZTSSe thin films. The XRD pattern of CZTSSe powder (Fig. 2(a)) exhibits a series of peaks corresponding to the (112), (200), (220), (312), (008)

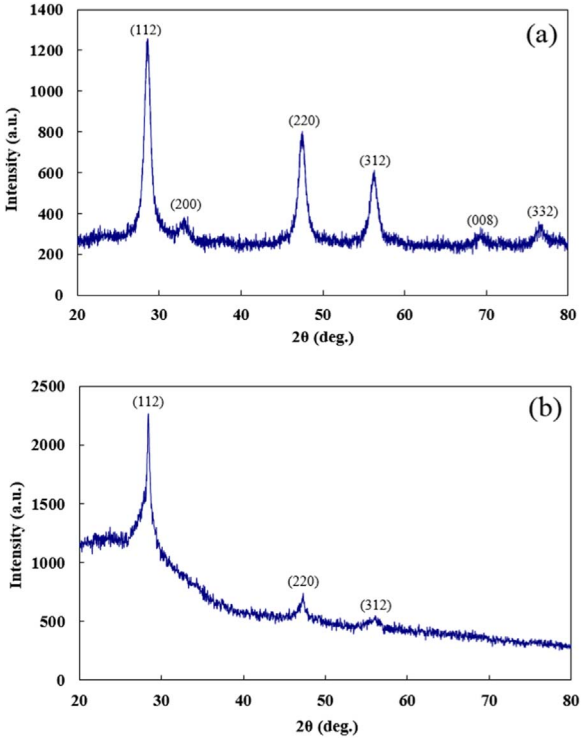

Fig. 2. XRD pattern of (a) sulfurized CZTSSe powder and (b) annealed CZTSSe thin film.