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Sputter grown sub-micrometer thick $\text{Cu}_2\text{ZnSnS}_4$ thin film for photovoltaic device application



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ABSTRACT

Structural properties and solar cells performance of sputter grown sub-micrometer thick (~ 600 nm) $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) films are investigated for low cost and large scale photovoltaic deployment. The CZTS films are deposited using single quaternary stoichiometric target at room temperature. X-ray diffraction, micro-Raman spectroscopy, and scanning electron microscopy measurements were carried out to investigate the structural property and secondary phase formation. The intense phonon peak at 334 cm^{-1} in the visible Raman spectra confirms the deposition of single phase CZTS films. CZTS-based thin film solar cells show excellent performance with open circuit voltage ~ 600 mV and over all cell efficiency of $\sim 3.07\%$, exhibiting commercial potential toward large scale fabrication of photovoltaic devices.

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1. Introduction

The quaternary semiconductor $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is an excellent p-type semiconductor for energy conversion applications. It has a high absorption coefficient of over 10^4 cm^{-1} in the visible wavelength region and a direct band gap of ~ 1.4 eV [1–3]. Unlike $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS), all the constituents of CZTS are low cost, non-toxic and earth abundant, leading to the possibility of cost effective solar cells [1,2]. The techniques for fabrication of CZTS thin films can be classified into two categories: vacuum based and non-vacuum based approaches. However, vacuum based techniques render highly uniform deposition and provide better opportunity for fabrication of high quality thin film devices.

There are enormous efforts reported to fabricate CZTS based thin film solar cells, in which the highest efficiency so far is $\sim 12\%$ [2]. However, according to the widely accepted Shockley–Queisser limit, an efficiency of 28% is possible to achieve with the CZTS solar cell [4]. In order to achieve efficiency closer to this limit, there are major challenges that need to be addressed. The major challenge in the construction of CZTS based solar cells is to develop impurity free, stoichiometric, and phase controlled absorber [5]. The structural, crystallographic, and electrical properties can be tailored by optimizing stoichiometry-compositions, which can

significantly control the formation of native defects. Since, defects as well as the small grain size of CZTS both shorten the diffusion length of carriers and increase the recombination rate, hence decrease the efficiency of the cell. Further, voids formed at interfaces due to bad adhesion between layers limit the device performances. At present, there is no clear idea about the formation mechanism of pure phase $\text{Cu}_2\text{ZnSnS}_4$. It is very difficult to fabricate single-phase $\text{Cu}_2\text{ZnSnS}_4$. Nagoya et al. performed first-principle studies of the phase stability and defect formation in CZTS [6]. It was found that the stable chemical potential region for the formation of stoichiometric and thermodynamically stable compound is very small. Even slight deviations from the optimal growth conditions will result in the formation of other sulphidic precipitates, including ZnS , Cu_2SnS_3 , SnS , SnS_2 , and CuS [6].

There are several reports on the sputter grown $\text{Cu}_2\text{ZnSnS}_4$ films [7–9]. A single-step sputtering from a quaternary $\text{Cu}_2\text{ZnSnS}_4$ compound target offers numerous advantages, including uniform composition of the thin film, smooth surface, simple process and highly reproducible. However, one quaternary target was rarely used in sputter deposition of CZTS due to deviation of the elemental composition between targets and thin films and the difficulty in controlling the stoichiometry of the films. Even though there are some reports available on the sputter grown CZTS, it is necessary to study the details structural property and secondary phase formation of the sputter grown CZTS using single

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quaternary target. Most of the photovoltaic devices reported in literature were fabricated using thick ($> 1 \mu\text{m}$) CZTS films. In this work, we have developed thin film ($\sim 600 \text{ nm}$) CZTS based solar cells by employing sputter grown absorber layer. The effects of sulfurization on single-step sputtered CZTS films are addressed and compared. The feasibility of manufacturing large area CZTS thin films solar cells from single-step sputtering is evaluated in this study.

2. Experimental

CZTS thin film was deposited on silicon (Si) substrate (100) and Mo-coated glass using RF magnetron sputtering at room temperature. After pre-cleaning, sputter deposition was carried out using a stoichiometric $\text{Cu}_2\text{ZnSnS}_4$ target with pure Ar gas as the sputtering gas with a base pressure of 10^{-7} Torr. The CZTS thin film was deposited with RF power of 150 W at a working pressure of 3.3 mTorr. The sputtered deposited CZTS films on silicon substrate were sealed in a quartz tube together with sulfur powder and were annealed in a furnace at 500–700 °C for 10 min. For the CZTS film Mo-coated glass, maximum annealing temperature was 650 °C. Scanning electron microscopy analysis, visible and ultraviolet Raman spectroscopy, and X-ray diffraction have been used to investigate the surface morphological features and crystal quality of sputter deposited CZTS thin film.

A CdS buffer layer with $\sim 60 \text{ nm}$ thickness was deposited on CZTS thin film after sulfurization by chemical bath deposition (CBD). Then 50 nm i-ZnO followed by 600 nm ZnO:Al layer were deposited by RF and DC magnetron sputtering. Finally silver glue was printed on AZO layer to form top contact fingers. Total area of the device is 0.16 cm^2 . Current density–voltage (J - V) curves for solar cells were performed using Xe-based light source solar simulator (VS-0852 and KEITHLEY 2612A) to provide simulated 1 sun AM 1.5 G illumination which was calibrated with a standard Si reference cell. The EQE were measured by PVE300 (Bentham) IPCE Instrument equipped with a xenon/quartz halogen light source and calibrated with Si/Ge reference detectors.

3. Results and discussion

Fig. 1 shows the XRD spectra of sputter grown CZTS films after

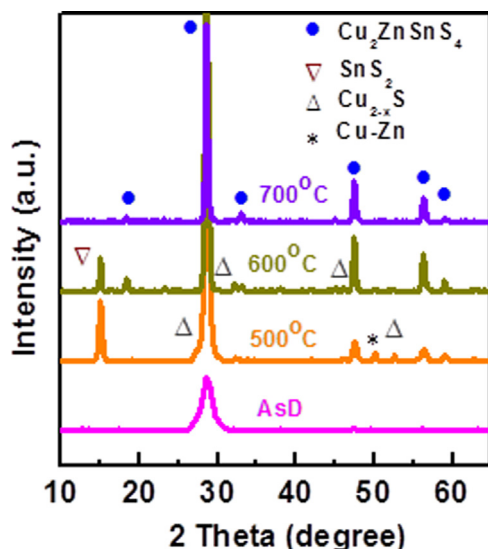


Fig. 1. XRD spectra of sputter grown CZTS on silicon substrates after thermal treatment at different temperatures.

thermal treatment at different temperatures. All films exhibit a major diffraction peak at 28.5° corresponding to (112) planes of kesterite CZTS phase [7]. The sputter grown as-deposited (AsD) CZTS shows formation of kesterite phase however peak is broad and the intensity is low, which suggests crystallinity of the film need to improve. The sulfur annealed films show much better crystallinity, which can be seen in the obvious increase in the sharpness of (112) peak and the appearance of other peaks that can be associated to CZTS. The peak intensity for CZTS increases with the increase of annealing temperature upto 600 °C, after that it decreases significantly. Formation of $\text{Cu}_2\text{-xS}$ can also be minimized by sulfur annealing. It is worth to note that there is a secondary phase of SnS_2 and Cu-Zn , which needs to be further eliminated for an improved device application.

Fig. 2 shows Raman spectra of CZTS samples using 488 nm and 325 nm laser line excitations. The spectra are recorded using a JY-LABRAM micro-Raman system. The optical phonon peaks are studied to investigate the effect of thermal treatment on phase formations in these CZTS films. The 325 nm ultraviolet Raman probes the nature of the surface due to a shallow probing depth. As shown in Fig. 2(a) and (b), the as-deposited film and samples on Si substrate after thermal treatment at different temperatures show well distinguishable Raman peaks associated with CZTS. A strong peak in all the samples is located at $\sim 334 \text{ cm}^{-1}$ in the 488 nm Raman excited spectrum which is known as the main vibrational A_1 symmetry mode from kesterite phase of CZTS [10]. The A_1 optical phonon peak arises from the vibrational modes related to S atom in the lattice where other atoms remain fixed and represent the formation of $\text{Cu}_2\text{ZnSnS}_4$. The much weaker peak at $\sim 288 \text{ cm}^{-1}$ which superimposed on a broad background related to SnS -like lattice vibration only observed for the sample annealed at 700 °C. The absence of this peak in samples annealed at 500–600 °C range manifests the formation of improved single phase CZTS. The phonon peak around $\sim 475 \text{ cm}^{-1}$ appears from the samples annealed at 700 °C and is attributed to the formation of Cu_{2-x}S [10,11], while this peak was much weaker in samples annealed at 500 and 600 °C. The higher energy shift of modes could be attributed to enrichment of S. The much broader shoulder peak at $\sim 350 \text{ cm}^{-1}$ is attributed to the cubic ZnS [12,13]. The linewidth of A_1 optical phonon peak at 334 cm^{-1} decreased after the thermal treatment showing the increase in the crystallinity in the samples annealed at higher temperatures. In the as-deposited film, this phonon line shows a lower energy asymmetry with broadening due to structural disorder related to random distribution of S atoms in the lattice. The asymmetry reduced at high temperature annealing where the shoulder peak at $\sim 350 \text{ cm}^{-1}$ also became weaker at 600 °C with respect to A_1 optical phonon peak. Thus, both the XRD and visible Raman studies confirm the improved CZTS structural quality in the layers subjected to thermal treatment.

As shown in Fig. 2(b), the UV Raman measurements which probe the surface states in these films reveals additional information related to lattice vibrations. The thermal annealing conditions are sensitive to surface disorder and related phase formation when no capping layer is deposited on CZTS. The as-deposited film shows weak and broad Raman modes in UV excitation at 285 and 325 cm^{-1} . The SnS -related sharp mode appears in UV Raman spectra at 285 cm^{-1} in samples annealed at 600 and 700 °C. The thermal annealing introduces a sharp Raman peak at 311 cm^{-1} which was too broad in visible Raman excitation to be resolved. The appearance of this peak reveals the lattice vibration related to the cubic phase Cu_2SnS_3 vibrations at the surface. In annealed samples, the mode related to CZTS A_1 vibration is sharp and appears as an overlapping shoulder peak at 335 cm^{-1} in UV Raman spectra. The phonon peak related to cubic ZnS -related vibration at 345 cm^{-1} is much stronger and shows a gradual peak

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