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Phase evolution pathways of kesterite Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ thin films during the annealing of sputtered Cu-Sn-Zn metallic precursors

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ABSTRACT

The formation of secondary phases in kesterite-based solar cells plays a critical role, affecting the performances of devices primarily due to the open circuit voltage deficient characteristics. Systematic studies of the phase evolution pathways and the formation of secondary phases in kesterite thin films are desirable. In this paper, the phase evolution pathways and the formation of secondary phases in kesterite Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) thin films during thermal treatment of sputtered Cu-Sn-Zn metallic precursors have been studied using high-resolution X-ray diffraction (XRD), Raman spectroscopy, field-emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). A possible phase evolution process for the kesterite thin films is proposed based on the experimental observations. The Cu-Sn-Zn metallic precursor thin films were prepared using the sputtering technique followed by thermal treatments at different temperatures ranging from 250 °C to 580 °C in a chalcogen atmosphere. XRD and Raman characterizations of the thin films annealed under chalcogen atmospheres indicated that the precursor thin films were completely transformed to the CZTS and CZTSe kesterite phases above 500 °C. However, the TEM analysis of the thin films annealed above 450 °C revealed Cu-based secondary phases. The formation of phase pure CZTS and CZTSe kesterites was observed at annealing temperatures above 500 °C. Based on the experimental observations, the phase evolution pathways for the formation of kesterite and secondary phases from metallic precursors are proposed in this paper.

1. Introduction

The kesterite Cu_2ZnSnS_4 (CZTS) and its related alloys $Cu_2ZnSn(S_x,Se_{1-x})_4$ (CZTSSe) are strong candidates for inexpensive and environmentally sustainable light absorbing materials due to their outstanding optical properties, high stabilities, and high theoretical efficiencies over 30% (Suryawanshi et al., 2013; Ghorpade et al., 2014). First, Katagiri's group conducted extensive pioneering studies on the synthesis of kesterite CZTS absorber thin films, and CZTS-based solar cells have achieved efficiencies of 6.77% using CZTS absorber thin films prepared via the sulfurization of co-sputtered precursors under a H_2S gas atmosphere (Katagiri et al., 2009). These results stimulated many research groups to realize low-cost and highly efficient thin film solar cells. Recently, Mitzi's group reported the highest efficiency for an ITO/ZnO/In_2S_3/CdS/$Cu_2ZnSn(S,Se)_4$ (CZTSSe) multi-structured TFSC of 12.7% using a hydrazine-based solution process (Kim et al., 2014). Although kesterite CZTS-based TFSCs have achieved rapid development in the research field, the highest obtained efficiency of 12.7% still limits the industrialization of CZTS-based TFSCs. The main cause of the poor performance of CZTS TFSCs compared with their theoretical values and those of commercially available TFSCs is the open circuit voltage (V_{oc}) deficient characteristic, which usually results from the high recombination rate in the p-n junction region, easy formation of secondary phases due to lower formation energies and the high intrinsic point defect density in kesterite compounds. Among these different parameters, the V_{oc} deficient characteristic due to the formation of secondary phases in the kesterite CZTS absorber layer plays a critical role that hampers the device

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efficiency. Generally, the secondary phases are temperature-dependent and usually formed in the surface and back contact regions of the kesterite thin films during thermal treatment due to their lower formation energies. The secondary phases located in the back contact region are attributed to the instability of the back contact and the oxidation state in tin (Sn) atoms during thermal treatment (Scragg et al., 2013; Li et al., 2014). They could be avoided by introducing chalcogenide diffusion barrier layers including i-ZnO, TiN, and TiB_2 leading to improved back contact stability (Li et al., 2014; Shin et al., 2012). In contrast to the back contact region, the $Cu_{2-x}(S,Se)$ and $Cu_2Sn(S,Se)_3$ secondary phases with conducting characteristics in the surface region may increase the recombination rate and generate a shunt current in the junction, thus quenching the electron-hole pairs (Scragg et al., 2011, 2012). Therefore, detailed understanding of the phase evolution pathway in CZTS and CZTSe films and the formation of secondary phases, as well as monitoring the locations of secondary phases, are desirable to improve the device performance by avoiding the formation of these secondary phases.

The previous studies on the phase evolution processes in terms of the phase transition from metallic or chalcogenide-containing precursors to kesterite CZTS thin films in a sulfur-containing atmosphere at functional temperatures have been carried out using traditional XRD and Raman spectroscopy techniques (Mainz et al., 2013; Schurr et al., 2009). Mainz et al. (2013) have reported a study of the phase transition from wurtzite nanorods to kesterite CZTS thin films using real-time energy dispersive XRD characterization. Additionally, Schurr et al. (2009) have demonstrated the phase evolution pathway of kesterite CZTS thin films from co-electrodeposited Cu-Zn-Sn metallic precursor thin films using in situ XRD. The main emphasis has been on the phase evolution from the precursor to kesterite compounds and further to the formation of pure kesterite phases, which is found to be a function of the annealing temperature. However, the phase characterizations using XRD and Raman techniques are not clear, especially in kesterite compounds, because they are quite similar to the crystallographic information for both kesterite CZTS(Se) and the secondary phases, such as ZnS(Se), SnS(Se), and $Cu_2SnS(Se)_3$ (CTS). In particular, the Raman analysis of CZTS thin films had a limited ability to distinguish the crystal structure due to the very short penetration depth (~100 nm) Shin et al., 2015; Suryawanshi et al., 2014; Gang et al., 2015; Inamdar et al., 2013. To solve this difficulty, clearly confirm the phase evolution pathway and observe the secondary phases in the kesterite compounds, one strong solution is transmission electron microscope (TEM) characterization. The detailed structural and chemical properties, interfaces, atomic level defects, grain boundaries, and phase separation in the absorber layer can be clearly investigated (Han et al., 2013; Jung et al., 2015). Furthermore, the locations of the secondary phase and indexing structures of each phase can be analyzed using the selected area electron diffraction (SAED) pattern and scanning TEM (STEM) techniques. This outstanding information can provide significant insight into understanding the phase evolution from precursors to kesterite, segregation of the secondary phase in kesterite and the performances of TFSCs. Recently, our previous paper successfully suggested the phase evolution pathway and formation of mechanism in the kesterite compounds by sulfurization of sulfur contained precursor thin films using detailed ex situ TEM characterizations (Han et al., 2013).

In this paper, the stacked Cu-Sn-Zn metallic precursor thin films were annealed under chalcogen atmospheres at different temperatures and characterized using ex situ TEM to clearly understand the phase evolution pathway in the kesterite thin films during the thermal treatment process. The phase evolution process at different annealing temperatures is proposed based on the experimental results during the annealing process.

2. Experimental details

The CZTS and CZTSe thin films were prepared by annealing stacked Cu-Sn-Zn metallic precursors, which were sequentially deposited on Mo-coated soda lime glass substrates (0.5 Ω/Sq., sheet resistance) by a direct current sputtering technique from Cu (99.999%), Sn (99.999%), and Zn (99.99%) targets (TASCO, Korea) at room temperature with a stacking order of Cu/Sn/Zn/Mo/soda lime glass. The $2.5 \times 2.5\ cm^2$ Mo-coated soda lime glass substrates were consecutively ultrasonically cleaned using acetone, methanol, isopropyl alcohol, and deionized water for 10 min, and then, the substrates were placed in the sputtering chamber. The sputtering conditions of each metallic layer were as follows: Cu ($0.68\ W/cm^2$, 8 mTorr, 1400 s), Sn ($0.68\ W/cm^2$, 8 mTorr, 960 s), and Zn ($0.68\ W/cm^2$, 8 mTorr, 660 s). The chamber was evacuated to a base pressure of 2×10^{-6} Torr, and then, the substrates were exposed to a plasma cleaning treatment. High purity Ar gas (99.999%) was used as the plasma source, and the gas flow rate was controlled using an MFC (mass flow controller) at 40 sccm. The stacked precursors and chalcogenide powders were placed in a graphite box ($12.3\ cm^3$) and annealed for 10 min. under functional temperatures ranging from 250 to 580 °C using a tubular

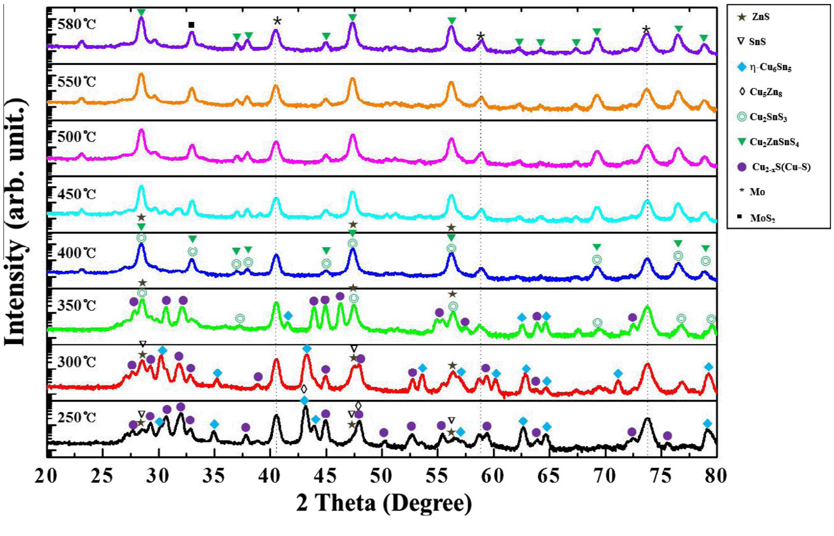

Fig. 1. The XRD patterns of the thin films sulfurized at different temperatures.

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