



Study of the fundamental phase formation mechanism of sol-gel sulfurized $\text{Cu}_2\text{ZnSnS}_4$ thin films using *in situ* Raman spectroscopy

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ABSTRACT

In the current work, the results of the *in situ* Raman monitoring of phase formation of copper zinc tin sulfide ($\text{Cu}_2\text{ZnSnS}_4$, CZTS) material from room temperature up to 350 °C are presented. Cu-Zn-Sn oxide precursors were sulfurized for up to 180 min using a 100 ppm $\text{H}_2\text{S} + 4\%\text{H}_2 + \text{N}_2$ gas mixture (by volume). The results showed that CZTS phase formed in about 30 min via a reaction between the metal oxide precursor film and the $\text{H}_2\text{S-H}_2$ gas mixture at intermediate temperature of 350 °C and remained stable upon extended exposure. In comparison, at lower temperature such as 170 °C, the oxide precursor film had to be reduced first (e.g., in 4% $\text{H}_2 + \text{N}_2$ forming gas) and then the CZTS phase emerged. However, continued sulfurization at lower temperature (e.g., 170 °C) led to the disintegration of CZTS and the formation of CuS impurity, which remains stable upon cooling the sample down to room temperature. The correlation between the *in situ* Raman monitoring data and the information from other *ex situ* characterization techniques provided useful information regarding the reaction pathways leading to the formation of sol-gel based CZTS thin films as well as other related phases under different sulfurization conditions. The outcomes of the current study also set the directions for optimizing the CZTS film structure and stoichiometry toward developing high performance CZTS solar cells in future.

1. Introduction

Copper zinc tin sulfide ($\text{Cu}_2\text{ZnSnS}_4$, CZTS) material has drawn great attention in the last decade as one of the most promising materials for thin film solar cells due to its elemental abundance, non-toxicity, and excellent optical and electronic properties comparable to the conventional Cu(In,Ga)Se₂ (CIGS) and CdTe thin film light absorber materials [1]. Many processing routes have been adopted for the preparation of CZTS thin films and they can generally be categorized as vacuum-based or solution-based. Vacuum-based deposition is typically carried out by evaporation [2,3] or sputtering [4] of metals (stacked in a certain order such as Zn/Sn/Cu) or binary sulfides (e.g., CuS, ZnS, and SnS) followed by high temperature (typically above 500 °C) annealing in a sulfur-rich or inert atmosphere. Besides system complexity and high cost, those vacuum-based processes represent challenges for industrial scaling up due to the high volatility of some elements and compounds (e.g., S and SnS_x) during the processing and the very narrow compositional region of the CZTS phase. In comparison, solution-based deposition techniques such as electrodeposition [5], spray pyrolysis [6], and sol-gel [7,8] offer simplified and low cost alternatives for the preparation of CZTS thin films. Among various solution-based processing routes, *sol-gel*

sulfurization, which involves the annealing of metal oxide precursor in a sulfur-rich atmosphere, is one of the simplest and cheapest options. It allows precise stoichiometry control on a molecular level during sol preparation and is able to achieve high quality crystalline thin films at lower annealing temperature [9].

Nevertheless, the preparation of high quality CZTS thin films for solar cell applications remained a challenge due to the intrinsic complexity of the multicomponent CZTS system [10]. Regardless of the processing route, there is a lack of understanding about CZTS formation and other side-reactions that might lead to various harmful secondary phases (e.g., ZnS, Cu_{2-x}S , and Cu-Sn-S) during processing, which contribute to the limited device efficiency. Such knowledge regarding the fundamental mechanism of CZTS formation and associated transformation is crucial to process optimization to obtain CZTS thin films with better quality and hence higher device performance.

To address this issue, several attempts have been made using different *ex situ* characterization techniques such as multiwavelength Raman scattering [11], Room Temperature Photoluminescence (RT-PL) [12], Secondary Ion Mass Spectroscopy (SIMS), and X-ray Spectroscopy (XPS) combined with SEM and EDS [13–15]. However, these techniques usually do *not* provide information regarding the real-time

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emergence and transformation of CZTS phase and other by-products. On the other hand, *in situ* XRD technique has been adopted to complement those *ex situ* techniques and provide useful information regarding the evolution of CZTS and other phases in real time [16,17]. However, XRD alone is not adequate in differentiating between CZTS and some closely-related phases such as ZnS and Cu_2SnS_3 (CTS) and it also suffers from poor spatial resolution [18].

In contrast, *in situ* Raman microspectroscopy, as a multiphase sensitive, non-destructive, and high spatial resolution (down to $\sim 1 \mu\text{m}$) tool, offers great potential to investigate the phase formation mechanism of CZTS material under real processing conditions and provide useful information regarding the process kinetics. Previous studies on CZTS using Raman spectroscopy were focused on structure transitions [19] and temperature influence up to only $\sim 100^\circ\text{C}$ on Raman peaks of CZTS thin films [20]. Recently, the authors of this work demonstrated that CZTS material is Raman active at elevated temperatures up to $\sim 600^\circ\text{C}$ and it would undergo significant oxidation in air starting from $\sim 400^\circ\text{C}$ [21]. Meanwhile, Wang et al. used *in situ* Raman to investigate the evolution of CZTS nanocrystals *via* the reaction between SnS_x , ZnS, and Cu_xS binary sulfide nanoparticles on a TiO_2 mesoscopic scaffold in nitrogen atmosphere [22], and found that kesterite-phase CZTS starts to form at 170°C under continuous heating condition.

However, to the best of our knowledge, there is no reported *in situ* Raman study for monitoring the phase formation of CZTS directly from sol-gel derived Cu-Zn-Sn oxide precursor in a sulfur-rich atmosphere. Therefore, the objective of the current study is to reveal the fundamentals about the phase formation process of CZTS thin films *via* sulfurization of Cu-Zn-Sn oxide precursor obtained by sol-gel processing in a hydrogen sulfide (H_2S)-containing atmosphere using the unique capability of the *in situ* Raman microspectroscopy technique. The insights from this study would also help optimize the formation of CZTS *via* sulfurization of sol-gel derived oxide precursor in parts-per-million or ppm-level H_2S at relatively low temperatures ($\sim 350^\circ\text{C}$ and below)

as developed in another work [23] by the authors aiming to produce CZTS thin films with superior quality *via* safe and low cost processing.

2. Materials and methods

The Cu-Zn-Sn metal oxide precursor thin films were prepared based on two different solutions: stoichiometric and Cu-rich. The reason for using the Cu-rich solution in the current study is that some reports recently suggest that Cu-rich CZTSSe films might offer denser layers and larger grains which is beneficial to the device performance [23,24].

The stoichiometric solution has Cu: Zn: Sn atomic ratio of 2: 1: 1 while the Cu-rich solution has Cu: Zn: Sn atomic ratio of 2.2: 1: 1 (*i.e.*, 10 at% Cu-rich). For stoichiometric solution, 4.37 g of copper acetate monohydrate (+99%, Sigma Aldrich), 2.40 g of zinc acetate dihydrate (+99%, Sigma Aldrich), and 2.47 g of tin chloride (+99%, Sigma Aldrich) were dissolved into 50 mL of 2-methoxyethanol (Afla Aesar) and the solution was stirred on a hot plate at 60°C for 1 h. 2 mL of monoethanolamine (MEA, Alfa Aesar) was also added to the solution to help dissolve the metal salts through the formation of complex intermediates. It also helps film adhesion and prevents defects (*e.g.*, voids and cracking) formation [25,26]. Then, the dark blue solution that formed was left to cool down to room temperature and filtered with $0.2 \mu\text{m}$ PTFE filter. After that, samples were prepared by spin coating on bare soda lime glass substrates at 3000 rpm for 30 s and air baked on a plate at 300°C for 5 min. The coating and air-baking steps were repeated 5 times to obtain the desired film thickness of $\sim 800 \text{ nm}$. The same procedure was adopted for the preparation of Cu-rich samples except for the starting amount of copper acetate monohydrate used was 4.78 g. Eventually, the oxide precursor samples were annealed in an H_2S -containing atmosphere in the *in situ* Raman monitoring cell that is specially designed for that purpose as described in detail below.

Fig. 1(a) shows a photo of the actual cell assembly used for the *in situ* Raman experiments and Fig. 1(b) is a top view photo without the

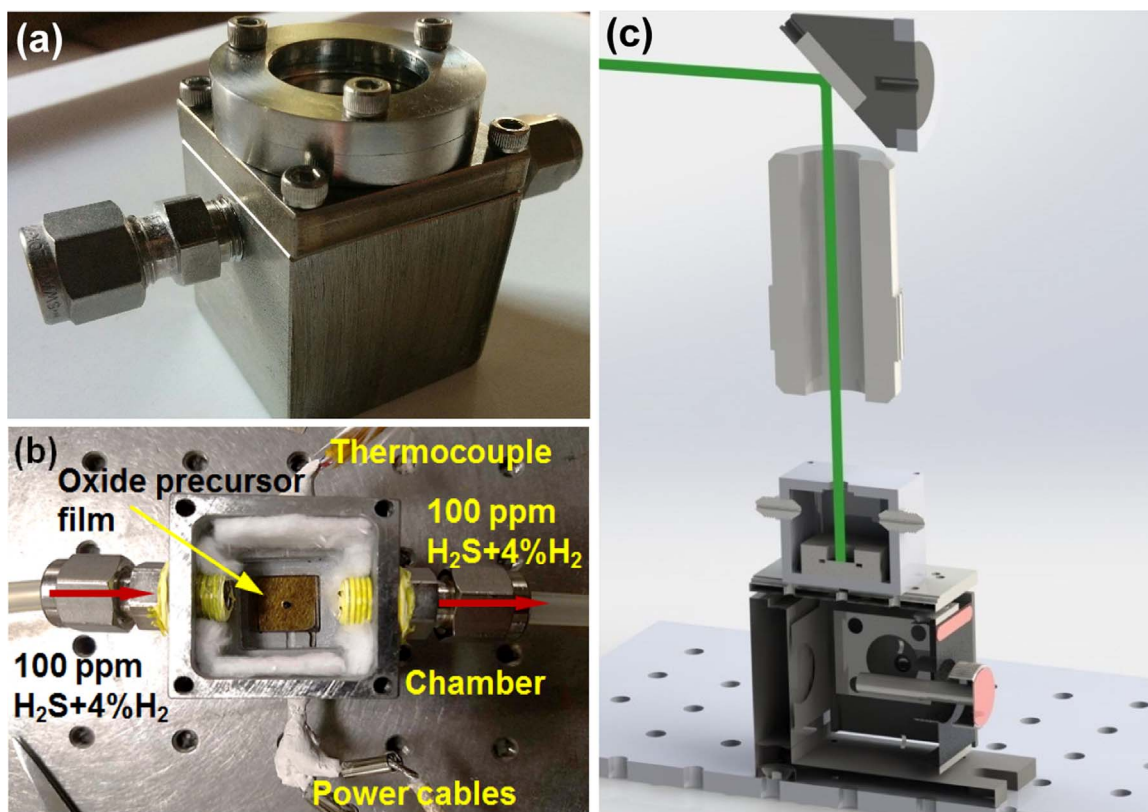


Fig. 1. (a) Photo of the actual *in situ* Raman cell used during the current study. (b) Top view of the actual *in situ* Raman cell with the top lid open showing the sample lying horizontally inside the cell and other gas and electrical connections. (c) Cross sectional model view of the *in situ* Raman cell assembled with the 3-axis stage and system optics.

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