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Growth of Cu_2ZnSnS_4 thin films by a two-stage process—Effect of incorporation of sulfur at the precursor stage

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ABSTRACT

The effect of sulfur incorporation at the precursor stage on the growth and properties of Cu_2ZnSnS_4 (CZTS) thin films prepared by a two-stage process is investigated. Two stacks, one with the precursor sequence ZnS/Sn/Cu and the other with an additional sulfur layer in the stack, were deposited sequentially by thermal evaporation onto soda-lime glass substrates held at 300 °C and annealed at two different temperatures, 550 °C and 580 °C, to understand the effect of inclusion of sulfur precursor layer at the precursor stage. These films were analyzed by studying their elemental composition, structural, microstructural and optical properties. CZTS films exhibiting kesterite structure with (112) preferred orientation are obtained. The lattice parameters are found to be $a = 0.542$ nm and $c = 1.089$ nm. The crystallinity and the grain size are found to increase with increase in annealing temperature. With the inclusion of sulfur precursor layer in the stack, CZTS growth occurred at the precursor stage itself. On annealing this stack at 550 °C for 30 min, CZTS films that consist of distinct and compact grains with size in the range 400–800 nm are obtained. Compared to this, the grain size of CZTS films obtained from the stack without sulfur layer in the precursor stage is found to be in the range 200–500 nm. The direct optical band gap of these films is found to be between 1.44 eV and 1.56 eV depending on the annealing temperature and duration.

1. Introduction

Kesterite family semiconductors, Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSnSe_4$ (CZTSe) and $Cu_2ZnSn(S,Se)_4$ (CZTSSe), with direct band gap (1.0–1.45 eV), high optical absorption coefficient ($\alpha > 10^4\ cm^{-1}$) and p-type electrical conductivity are emerging as potential solar cell absorber layers. Their suitable properties and relatively non-toxic, abundant constituent elements make them attractive alternatives to $Cu(In,Ga)Se_2$ (CIGS), a proven solar cell absorber layer which contains expensive and scarce elements like In and Ga that may pose a problem in the long run for high volume production at affordable cost. CZTS, CZTSe and CZTSSe based thin film solar cells have exhibited efficiencies of 8.4% [1], 9.15% [2] and 12.6% [3] respectively, but these are quite low compared to the record efficiency of 20.8% [4] of CIGS cells. Thus a lot of further understanding of the film growth, formation mechanism, control of composition, morphology, other basic properties of these kesterite absorbers as well as interface properties of these cells is very much essential to improve the efficiency further.

Among these kesterite absorbers, CZTS ($E_g = 1.45$ eV) is explored to a greater extent. Various PVD techniques, like evaporation [1,5–8], sputtering [9,10], pulsed laser deposition [11], two-stage process (precursor formation + sulfurization) [12–22] and chemical approaches like spray pyrolysis [23–25], electrodeposition [26], sol–gel [27,28], and SILAR [29], have been used to grow CZTS films and understand their properties. Of these, two-stage process is relatively advantageous due to its scalability and high throughput. In this case, precursors are deposited onto substrates held at room temperature (RT) or a little higher by DC magnetron sputtering [16,21], RF sputtering [14,22], electron beam evaporation [12,13,15,17], electrodeposition [18–20], etc. and subsequently annealed at 500–600 °C under sulfur atmosphere to obtain CZTS films. The reported annealing duration is about 3–7 min in case of rapid thermal annealing [30,31] and varies from half an hour to 8 h in case of isothermal annealing [13,30,32,33].

Ramp rate, dwell time and cooling period of the annealing process play an important role in achieving good grain growth, morphology and compositional homogeneity in the films. Increase in the annealing/sulfurization duration of the stack is expected to improve depth-wise homogeneity of the films. However, a long annealing/sulfurization duration hinders process throughput and may result in Zn or Sn loss [13,34,35] if sulfur partial pressure is insufficient due to gradual consumption of the loaded sulfur mass. Hence suitable growth and annealing strategies need to be explored to arrive at optimal growth/annealing conditions while simultaneously achieving the desired micron sized grains with

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lateral, depth-wise compositional and morphological homogeneity. This is expected to minimize the inter-grain boundary losses in the absorber layer. Grain sizes reported in the two-stage process by different groups fall in the range 0.1–1.5 μm [31,32,36].

The objective of this work is to examine whether the inclusion of sulfur as a precursor layer in the first stage itself leads to CZTS nucleation/formation and to determine whether annealing duration required to obtain reasonable grain growth can be reduced. Instead of depositing the precursor layers at room temperature (RT) as is usually done, a substrate temperature of 300 °C was chosen to promote inter-diffusion of the precursor layers during the first stage. The first part of this paper deals with the growth of CZTS films using a stack wherein sulfur precursor layer is not included in the precursor stage and the second part of the paper deals with the growth of CZTS with inclusion of sulfur precursor layer in the stack. For each stack, with and without sulfur layer in the precursor stage, the effect of annealing/sulfurization temperature on the compositional, structural, microstructural and optical properties was investigated.

2. Experimental details

Two stacks, one with the precursor layer sequence, ZnS/Sn/Cu/ZnS/Sn/Cu (Stack-A) and the other with the precursor layer sequence ZnS/Sn/Cu/S/ZnS/Sn/Cu/S (Stack-B, with inclusion of sulfur as another precursor layer), were prepared in order to understand the effect of inclusion of sulfur as another precursor layer in the first stage on the growth of CZTS films by a two-stage process. Instead of depositing thick precursor layers of ZnS, Sn and Cu with the desired thickness in the stack, two precursor layer sequences, ZnS/Sn/Cu/ZnS/Sn/Cu, each with half the thickness than that in a single sequence ZnS/Sn/Cu were deposited. This is done to allow easy inter-mixing/diffusion of the precursors to obtain homogeneity on annealing. These layers were deposited by thermal evaporation onto chemically and ultrasonically cleaned soda-lime glass substrates held at 300 °C. Spectroscopically pure ZnS, Sn, Cu and S (Sigma-Aldrich, USA), kept in molybdenum boats, were used as the source materials in a 4-source vacuum coating unit (Hind High Vacuum Private Ltd, INDIA, Model: BC-300) for the deposition of the precursor layers. Sulfur source was used only for the deposition of its layers in Stack-B. Prior to evaporation, the substrates were cleaned by ion bombardment in the vacuum chamber. The precursor layers thicknesses were so chosen to compensate for the Zn and Sn losses expected at higher deposition/annealing temperatures and to obtain Cu-poor and Zn-rich CZTS films needed for the device fabrication. The base pressure of the vacuum chamber was 4×10^{-6} mbar and the working pressure was 5×10^{-5} mbar. During the deposition, the substrate holder was rotated using a rotary drive mechanism for uniform deposition of the precursor layers. Immediately after the deposition, the substrates were allowed to cool naturally to room temperature.

In the second stage, the stacks were annealed in sulfur atmosphere at 550 °C and 580 °C in a two-zone tubular furnace to study the effect of annealing temperature. The stack to be annealed was kept in one zone on a graphite block and sulfur pellets (99.998% Sigma-Aldrich, USA) in molybdenum boat were kept in another zone. The temperature of each zone could be controlled independently using proportional integral derivative (PID) controllers. Rotary pump was used to evacuate the quartz tube initially. Nitrogen was used as the carrier gas and the desired pressure in the tube was maintained using a needle valve at the gas inlet and a control valve connected to the rotary pump. The (N_2 + S_2) pressure was kept to be 100 mbar. Stack-A temperature was increased at the rate of 20 °C/min up to 300 °C and at the rate of 5 °C/min thereafter till the annealing temperature was reached to allow sulfurization to take place. The substrates were held at the annealing temperature for 90 min. In the case of Stack-B which contains sulfur as one of the precursor layers, the ramp rate was increased to 50 °C/min to reach the desired annealing temperature since the sulfur was already included in the first stage. Three annealing durations, 10, 30 and 60 min, were tried to understand how the CZTS film growth progresses. In both the cases, sulfur source ramp rate was chosen such that the vapors were available when the sample temperature reaches 350 °C to minimize the Zn/Sn losses. After the annealing process, the samples were allowed to cool naturally to room temperature.

The films were analyzed by studying their elemental composition, structural, microstructural and optical properties. The thickness of the films was determined using a Tencor stylus profilometer (Tencor P-20 H). X-ray diffraction (XRD) patterns of the films were recorded using computer controlled X-ray diffractometer (BRUKER, Model: D8 Advance) in the 2θ range 10–60° with CuK_α radiation (λ= 0.15406 nm). Raman spectra were recorded using Horiba Jobin Yvon HR 800UV confocal micro-Raman spectrometer in the backscattering mode. Nd:YAG laser source (λ=532 nm) of power 20 mW, spot diameter of ~1 μm and a 1800 lines/mm grating were used. Surface morphology and elemental composition were obtained using field emission scanning electron microscope (FESEM) (Carl Zeiss, Model: ULTRA-55) attached with an energy dispersive spectrometer (EDS, Oxford Instruments, U.K). Spectral transmittance and reflectance of the films were recorded on UV–Vis–NIR double beam spectrophotometer (Perkin Elmer, Model-LAMDA 950) in the wavelength range 300–2500 nm.

3. Results and discussion

3.1. Stack-A: effect of annealing temperature on CZTS film growth

3.1.1. Composition

Table 1 shows the elemental composition of films obtained on annealing Stack-A at 550 °C and 580 °C under 100 mbar pressure for 90 min. The uncertainty in the determination of elemental composition by EDS analysis is ±5 at%. The films are slightly Cu-poor. The relative variation in the Cu/(Zn+Sn) and Zn/Sn ratios is from 0.95 to 0.92 and 1.01 to 0.96 respectively with increase in the annealing temperature.

3.1.2. Structural analysis

(a) *X-ray diffraction analysis*: Fig. 1 shows the X-ray diffraction (XRD) patterns of films obtained on annealing Stack-A at 550 °C and 580 °C. The observed diffraction peaks match well with CZTS standard data (JCPDS No. 26-0575). The films are found to exhibit kesterite structure with (112) preferred orientation. The intensity of the peaks increases and full width at half maximum (FWHM) decreases with the increase in annealing temperature indicating improvement in crystallinity. Secondary phases CuS, Cu_2S, SnS, SnS_2, Sn_2S_3, Cu_3SnS_4 and Cu_4SnS_4 are unlikely as the most intense peaks due to these phases are not seen within the detection limit of XRD. But it is quite difficult to rule out the presence of Cu_2SnS_3

Table 1
Elemental composition of films obtained on annealing Stack-A at 550 °C and 580 °C.

T_A (°C)	Atomic percent				Ratio		
	Cu	Zn	Sn	S	Cu/(Zn+Sn)	Zn/Sn	S/M
550	23.9	12.6	12.5	50.9	0.95	1.01	1.04
580	22.9	12.2	12.7	52.2	0.92	0.96	1.09