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Synthesis of wittichenite Cu_3BiS_3 thin films by sulfurizing thermally evaporated Cu-Bi metallic stacks

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Wittichenite Cu_3BiS_3 thin films have received significant interest as light harvesters owing to their suitable optoelectronic properties and presence of earth-abundant, and non-toxic elements. We have synthesized Cu_3BiS_3 thin films by a two-stage process; in which, Cu/Bi/Cu metallic stacks were thermally evaporated and then sulfurized at 400 ^oC for 10–60 min in a quartz tubular furnace. The influence of sulfurization time on the structural, microstructural, compositional, optical, and electrical properties of the films was investigated. The results revealed that the films were orthorhombic Cu_3BiS_3 with the following lattice parameters: a = 0.768 nm; b = 1.043 nm; and c = 0.674 nm. Films uniformity, compactness, and crystal grain size increased upon increasing the sulfurization duration. On increasing the sulfurization time, the elemental stoichiometry of the films improved, and the direct optical bandgap increased from 1.38 to 1.40 eV. Additionally, Cu_3BiS_3 films exhibited p-type electrical conductivity and the electrical resistivity decreased with the increasing sulfurization time. Consequently, the Cu_3BiS_3 films synthesized at 30- and 60-min sulfurization durations can be applied to thin-film solar cells.

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1. Introduction

Recently, ternary compound semiconductor thin films belonging to the I-V-VI family have been investigated for applications in the fields of optoelectronic devices, solar cells, photo electrochemical cells, optical imaging devices, and infrared sensors. Among these, $CuSbS_2$, $CuSbSe_2$, $AgSbS_2$, Ag_3SbS_3, $AgBiS_2$, Cu_3BiS_3, and Cu_3BiSe_3 have shown the highest potential [1–6]. Solar cells based on $Cu(In,Ga)Se_2$, CdTe, perovskite, and $Cu_2ZnSn(S,Se)_4$ occupy the largest share of the photovoltaic market owing to their higher efficiencies [7]. However, even these best performing devices have certain disadvantages, such as high cost, scarcity, stability, and toxicity. These disadvantages motivated the search for alternative materials that can meet the requirements of solar cell materials. Cu_3BiS_3 with a wittichenite crystal structure fulfils several essential requirements for a thin film solar cell absorber. Cu_3BiS_3 has a direct optical bandgap of 1.42 eV (close to the optimum bandgap for efficient energy conversion), and high optical absorption coefficient in the visible

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region ($\alpha \geq 10^4$ cm^{-1}), displays p-type electrical conductivity, and is formed from the earth-abundant precursor elements.

Various physical and chemical deposition methods have been used to synthesize Cu_3BiS_3 thin films, including thermal evaporation [8–11], sputtering [12], a two-step method [13–17], spray pyrolysis [5, 18], chemical bath deposition [19, 20], spin coating [6, 21, 22], and electrodeposition [23]. The two-step method has a significant advantage compared to the rest because of its scalability and higher throughput. In this two-step method, the formation of Cu_3BiS_3 films can be achieved by sulfurizing CuS/Bi [13], Bi_2S_3/Cu [14], Cu_2S/Bi_2S_3 [16], or Cu/Bi [15, 17] precursors layers. In the present study, we synthesized Cu_3BiS_3 films by depositing metallic layers of Cu/Bi/Cu in the first step, followed by sulfurization at 400 ^{o}C for 10–60 min in the second step. The films exhibited exceptional structural, microstructural, optical, and electrical properties that are suitable for a photovoltaic absorber.

2. Experimental methods

Cu_3BiS_3 thin films were fabricated onto soda-lime glass (SLG) substrates by sulfurizing thermally evaporated Cu-Bi-Cu metallic layers. The substrates were cleaned by soaking overnight in chromic acid followed by washing with a soap solution. The SLG was then ultrasonically washed with acetone, ethanol, and deionized water. The washed glass substrates were placed in a vacuum chamber, which was evacuated to 2×10^{-6} Torr base pressure. Elemental Cu and Bi of 4N purity were used as starting materials for evaporation. The Cu and Bi metallic layers were evaporated with a sequence of Cu/Bi/Cu to promote easy intermixing during sulfurization. The Cu precursor was deposited at 3 $\mathring{A}/s$, followed by the deposition of Bi (260 nm) at 3 $\mathring{A}/s$, and another deposition of Cu (130 nm). The deposition was performed at room temperature and the substrates were rotated to obtain uniform layers. The thickness of the layers was measured using a thickness monitor. The sequentially evaporated Cu/Bi/Cu metallic stacks were sulfurized at 400 ^{o}C for 10–60 min in a quartz tubular furnace for their conversion into Cu_3BiS_3 films [24, 25].

The structural, morphological, elemental, optical, and electrical properties of the synthesized Cu_3BiS_3 films were analyzed by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDS), UV-Vis-NIR double beam spectrophotometry, and a Hall system [24, 25]. A PANalytical X-ray diffractometer (XRD) with a Cu K_α (0.15406 nm) source in the grazing incidence ($\omega = 3^o$) mode was used to determine the structural properties of the films. A field emission scanning electron microscope (FESEM; Hitachi S-4800) was used to record the surface morphology of the films. An energy dispersive X-ray spectroscopy (EDAX) was used to determine the elemental composition of the films. A Cary 5000 UV-Vis-NIR double beam spectrophotometer was used to record the spectral transmittance of the films in the range of 300–2500 nm. An ECOPIA Hall measurement system (HMS-3000, VER 3.53) was used to determine the electrical properties of the films.

3. Results and Discussion

3.1. X-ray diffraction

The XRD patterns of the Cu_3BiS_3 films synthesized by sulfurizing the Cu/Bi/Cu layers at 400 ^{o}C for 10–60 min are shown in Fig. 1. The XRD pattern of the film synthesized at 10 min sulfurization duration exhibit peaks corresponding to Cu_3BiS_3 (JCPDS card No. 43-1479). The crystal structure of the film is determined to be orthorhombic with lattice parameters a = 0.768 nm, b = 1.043 nm, and c = 0.674 nm, which agree well with the reported lattice parameters of Cu_3BiS_3. The XRD patterns of the films synthesized at 30- and 60-min durations did not show considerable variation in their peak positions. However, the peak broadening of the intense (031) peak decreased from 0.3936^o to 0.3444^o, corresponding to an increase from 55 to 61 nm [26] in the crystallite size of the films upon increasing the sulfurization duration.

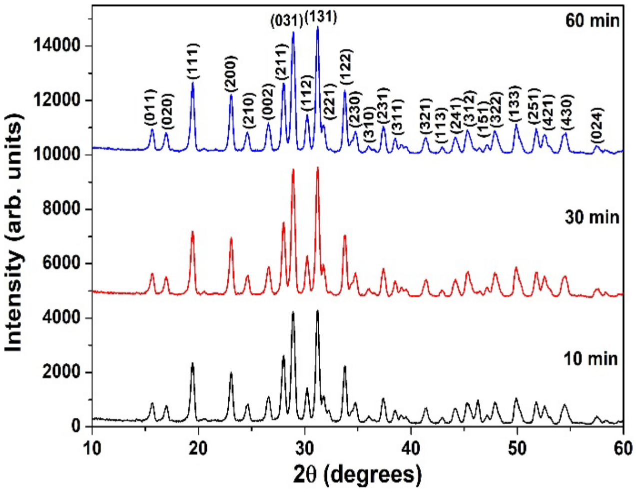

Fig. 1. XRD patterns of the Cu_3BiS_3 films synthesized by sulfurizing the stacks at 400 °C for 10–60 min.

3.2. Morphology

The surface morphologies of the synthesized Cu_3BiS_3 films are shown in Fig. 2. The micrograph of the Cu_3BiS_3 film synthesized at 10 min sulfurization duration reveals the formation of a uniform and compact films with distinct shaped grains 1.0–2.5 μm in size. The micrograph of the film synthesized at 30 min duration showed improvements in uniformity, compactness, and grain size to 2.0–2.5 μm. The further increase of the sulfurization duration to 60 min resulted in an improvement in film morphology and increase in the grain size to 2.0–4.0 μm.

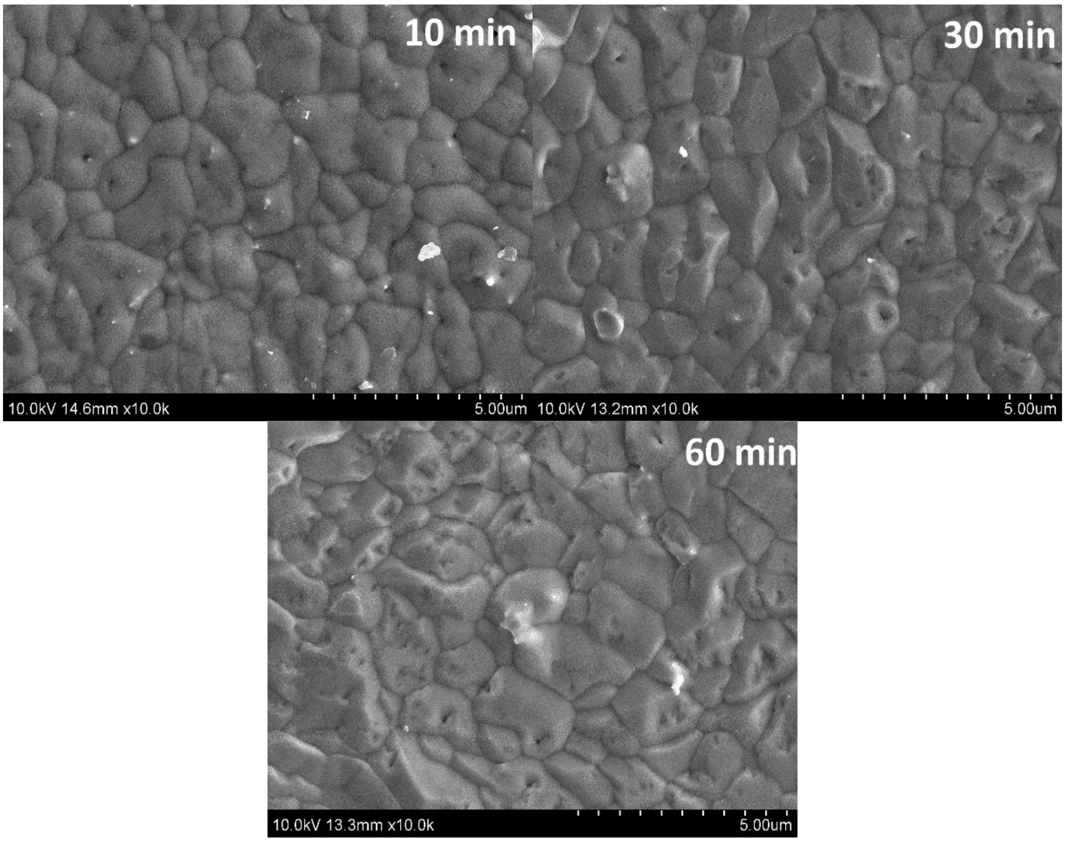

Fig. 2. FESEM images of the Cu_3BiS_3 films synthesized by sulfurizing the stacks at 400 °C for 10–60 min.

3.3. Elemental composition

The elemental compositions of the Cu_3BiS_3 films synthesized at different sulfurization durations are listed in Table 1. The near-stoichiometric atomic percentages of Cu, Bi, and S in Cu_3BiS_3 were determined to be 42.85, 14.30, and 42.85%, respectively. The films synthesized at 10 min duration exhibit a Cu-poor, Bi-poor, and S-rich composition due to the incomplete intermixing of the elements in this short duration. Upon increasing the sulfurization duration to 30 min, the atomic ratios of the films become near-stoichiometric owing to the complete intermixing of the elements and the complete formation of Cu_3BiS_3. Further increase in the sulfurization time to 60 min results in a slight variation in the elemental composition owing to the slight material loss in the longer duration of sulfurization. The Cu/Bi and S/(Cu+Bi) ratios in the films varied with sulfurization duration from 2.77 to 3.47 and from 0.69 to 0.98, respectively.

Table 1. Elemental composition of the Cu_3BiS_3 films synthesized by sulfurizing the stacks at 400 °C for 10–60 min.

Sulfurization		At. (%)		Ratio	
time	Cu	Bi	S	Cu/Bi	S/(Cu+Bi)
10 min	39.2	11.3	49.5	3.47	0.98
30 min	43.5	15.7	40.8	2.77	0.69
60 min	43.8	14.6	41.6	3.00	0.71

3.4. Optical absorption

The optical transmittance curves of the Cu_3BiS_3 films synthesized at different sulfurization durations are shown in Fig. 3. The Cu_3BiS_3 film synthesized at 10 min duration exhibited ~20% transmittance at longer wavelengths owing to the S-rich nature of the films. The film exhibits a shift in the onset of absorption from 1050 nm to 850 nm corresponding to the formation of Cu_3BiS_3 [8, 12, 13, 16]. The films synthesized after sulfurizing the stacks at 30 and 60 min show increased transmittance of up to ~50% and the onset of absorption is blue shifted due to the improved crystallinity of the films.

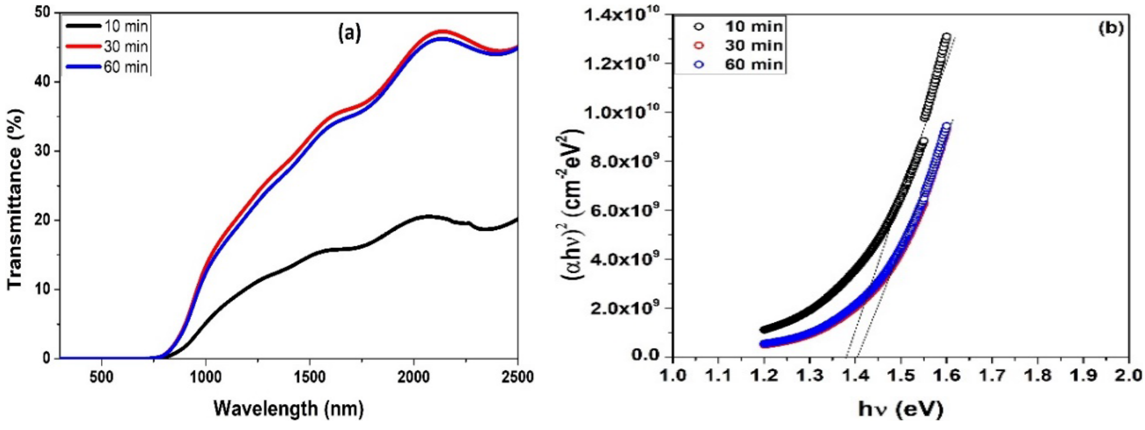

Fig. 3. (a) Spectral transmittance and (b) $(\alpha h\nu)^2$ versus hν curves (Tauc plots) of the Cu_3BiS_3 films synthesized by sulfurizing the stacks at 400 °C for 10–60 min.

The Tauc plots were drawn by determining the optical absorption coefficient (α_λ) using the relation, $\alpha_\lambda = \ln(1/T_\lambda)/t$, where 't' is the film thickness. Fig. 3(b) corresponds to the Tauc plots of the Cu_3BiS_3 film synthesized at different sulfurization durations. From the Tauc plots, the direct bandgap of the Cu_3BiS_3 synthesized at 10 min duration is determined to be 1.38 eV. The direct bandgap of the films synthesized with increasing sulfurization duration to 30 and 60 min increases to 1.4 eV. The determined value of 1.4 eV matches the reported bandgap of Cu_3BiS_3 [8, 12, 13, 16].

3.5. Electrical properties

The electrical properties of the Cu_3BiS_3 films synthesized at different sulfurization durations are listed in Table 2. The films synthesized at three different durations exhibit a positive Hall co-efficient owing to the p-type electrical conductivity. The film synthesized at 10 min duration exhibits an electrical resistivity of 72.5 Ωcm, hole mobility of 4.28 $cm^2V^{-1}s^{-1}$, and carrier concentration of 1.71×10^{16} cm^{-3}. Upon increasing the sulfurization duration from 30 to 60 min, the electrical resistivity and hole mobility decreases from 53.5 to 34.1 Ωcm and from 4.99 to 4.45 $cm^2V^{-1}s^{-1}$, respectively, whereas the carrier concentration increases from 2.33×10^{16} to 4.71×10^{16} cm^{-3}. The decreased electrical resistivity with increased sulfurization duration can be attributed to the reduced S content in the films and increased crystallinity.

Table 2. Electrical properties of the Cu_3BiS_3 films synthesized by sulfurizing the stacks at 400 °C for 10–60 min.

Sulfurization time	Resistivity (Ωcm)	Mobility ($cm^2V^{-1}s^{-1}$)	Concentration (cm^{-3})
10 min	72.5	4.28	1.71×10^{16}
30 min	53.5	4.99	2.33×10^{16}
60 min	34.1	4.45	4.71×10^{16}

4. Conclusions

We developed Cu_3BiS_3 thin films by sulfurizing Cu/Bi/Cu metallic layers at 400 °C for 10–60 min and investigated the influence of the sulfurization duration on the formation of Cu_3BiS_3 films. The Cu_3BiS_3 films synthesized at 10 min of sulfurization duration exhibited an orthorhombic crystal structure with a grain size of 1.0–2.5 µm, a metal-poor and S-rich elemental composition, a direct optical bandgap of 1.38 eV, and an electrical resistivity of 72.5 Ωcm. The increase in the sulfurization duration from 30 to 60 min improved the crystallinity and stoichiometry, increased the grain size (2.0–4.0 µ), and optical bandgap (1.4 eV), and decreased the electrical resistivity (34.1 Ωcm).

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