

Research Article

Growth of CZTS Thin Films by Cosputtering of Metal Targets and Sulfurization in H₂S

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Copper zinc tin sulfide (CZTS) is an emerging thin film photovoltaic material. Chemical composition and phase purity are important factors which decide the quality of the film for photovoltaic applications. In the present work, we report the results of the morphological, structural, optical, and electrical characterizations of Cu₂ZnSnS₄ thin films, synthesized by sulfurizing magnetron cosputtered Cu₂ZnSn thin films in ambient H₂S. To the best of our knowledge, this is the first report on CZT deposition by cosputtering from Cu, Zn, and Sn targets and sulfurizing it in ambient H₂S for making CZTS thin films. GIXRD and Raman study results showed that the film was kesterite CZTS. Optical absorbance studies revealed a band gap value of ~1.5 eV for CZTS thin film. Results of the Hall effect measurements are also reported.

1. Introduction

Copper zinc tin sulfide (CZTS) is an emerging thin film solar photovoltaic absorber material and is composed of earth abundant, nontoxic, and cheaper materials. It is a semiconductor with a direct band gap of about 1.5 eV and an absorption coefficient of $\sim 10^4 \text{ cm}^{-1}$ [1]. Therefore, a thickness of 1-2 μm is sufficient for absorbing the solar radiation. It is a good substitute for copper indium gallium selenide (CIGS) solar photovoltaic absorber, which is composed of rare, costly and relatively toxic materials. A record efficiency of 20.3% has been recorded for CIGS solar cell [2]. There are many issues which need to be answered in order to improve the stability and other characteristics of the solar cell. As both CZTS and CIGS solar cells have similar physics working for them, it is economical to carry out detailed research on CZTS [3]. In order to commercialize CZTS thin film solar cell, its efficiency needs to be enhanced. The highest reported efficiency of CZTS solar cell by Todorov et al. is ~11.1% [4]. Different methods for synthesizing CZTS absorber materials have been reported in the literature [5–18]. The methods include thermal evaporation [5], sputtering from metal targets (layer by layer) [6], sputtering from sulfide or composite targets [7], pulsed-laser depositions [8], chemical methods (sol-gel

[9], electrodeposition [10], and nanocrystals synthesis [11]. Among the physical vapor deposition techniques, sputtering is widely used in industry. Although, stoichiometric films can be deposited using PLD, small substrate size is its limitation. Composition of the film plays an important role in determining the efficiency of the solar cell. As different elements have different sputter rates, sputtering using CZTS alloy targets may not permit the necessary control over the composition of the CZTS film. CuS, ZnS, SnS, and so forth are some of the common secondary phases that can nucleate while synthesizing CZTS thin films. The presence of secondary phases may act as recombination centers in the solar cell and can degrade the quality of the cell. In this study, Cu₂ZnSn thin films have been synthesized by cosputtering Cu, Zn and Sn targets. This gave the freedom to control the amount of different metals individually by controlling the sputtering power. The Cu₂ZnSn film has been sulfurized in ambient H₂S in order to obtain CZTS thin films. A summary of sputtering methods used for depositing the CZTS films, sputtering target used and the sulfurization conditions used in the literature is presented in Table 1 [7, 8, 12–18]. From the table, it is clear that this is the first report on the synthesis of Cu₂ZnSn thin films by cosputtering from Cu, Zn, and Sn metal targets and carrying out sulfurization in ambient H₂S.

TABLE 1: Different sputtering methods used for depositing CZTS thin films.

Sputtering methods	Targets	Sulfurization conditions	References
RF cosputtering	Cu, ZnS, SnS	H ₂ S (20%) + N ₂ at 580°C for 3 h	[7]
RF sputtering	CZTS (sintered with Cu ₂ S : ZnS : SnS ₂ = 1 : 1 : 1)	Annealed at 400°C/30 min during deposition	[8]
Dc reactive sputtering	Cu : Zn : Sn = 2 : 1 : 1 (H ₂ S + Ar) at 500°C for 60 min	—	[12]
Sputtering (layer by layer)	Cu, Zn, Sn	S at 250°C, film at 570°C for 20 min	[13]
RF cosputtering	Cu ₂ S, ZnS, SnS ₂	Ar + S ₂ (g) at 250–400°C for 1 h	[14]
RF cosputtering	CuSn (60 : 40), ZnS	S (2 mg) at 520°C for 1 h	[15]
Reactive sputtering (50% H ₂ S/Ar)	Cu, Zn, Sn	Annealed at 40 mtorr, 550°C 10% H ₂ S/Ar mixture	[16]
Simultaneous RF sputtering	Cu ₂ S, ZnS, SnS ₂	Annealed under sulfur vapor; sulfurization temp was 550, 600, and 650°C	[17]
Simultaneous (DC, RF) sputtering	Cu, ZnS, SnS	H ₂ S diluted with 97% N ₂ , annealed at 500°C for 10 min	[18]

It should be noted that Yoo and Kim have also used three different metal targets for depositing metallic films, but they have made stacked/layered films [13]. In the present study, all the three targets have been sputtered simultaneously. It has been shown that the presence of any metal in excess may lead to the formation of secondary phase and stoichiometric film can be obtained only if the initial composition is controlled. The morphological analysis has been carried out using the SEM, and the chemical compositional analysis has been carried out using EDS attached with SEM. Structural analysis has been carried out using XRD, HRTEM, and Raman spectroscopic studies. The optical properties have been characterized using the UV-Vis spectrophotometer. Temperature-dependent electrical conductivity study has also been carried out in order to calculate the activation energy. The type of carrier, carrier concentration, and so forth have been evaluated using the Hall effect measurements.

2. Experimental Details

In order to deposit copper zinc tin (Cu₂ZnSn) thin films, Cu, Zn, and Sn have been cosputtered from their metal targets. The depositions have been carried out in a magnetron sputtering system having arrangements for mounting three two-inch targets confocally. All three magnetron guns can be tilted $\pm 15^\circ$. An ion gun is mounted for final cleaning of the substrates. The system has substrate rotation as well as substrate heating facility. It is automated through a PLC-PC-based automation system. In the present work, copper (99.999%) has been deposited using DC power; Sn (99.999%) and Zn (99.995%) have been deposited using RF power. The thickness of the individual metal can be controlled by controlling the power. In all the experiments, substrate temperature was 430 K and substrate rotation was 10 rpm. Prior to sputter deposition, a base pressure of $\sim 9.0 \times 10^{-7}$ mbar was achieved using a turbomolecular pump (800 L/s). The depositions were carried out at a working pressure of 5.2×10^{-3} mbar with an argon flow rate of 80 sccm. Soda-lime glass (thickness 0.7 mm) substrates were first cleaned in warm soap solution.

Then, they are ultrasonicated in acetone/alcohol/deionized water successively. Finally, they were dried in nitrogen flow. Sulfurization was carried out in a horizontal tube furnace fitted with quartz tube. At one end of the tube, gas supply arrangements were there, and on the other end, a rotary pump was fitted to pump down the system. CZT film was kept on an alumina holder at the centre of the furnace. The system was evacuated to 2×10^{-2} mbar and flushed with nitrogen in order to remove any oxygen content. The sulfurization was carried out in the presence of H₂S gas (diluted with 85% Argon). The H₂S flow rate was 12.5 sccm (controlled by mass flow controller). The furnace was heated to 400°C in 10 min and then to 550°C in next 10 min and was kept at 550°C for 25 min. Then, it was allowed to cool down to room temperature. The outgoing gas was passed through aqueous KOH.

Glancing incidence X-ray diffraction studies of the thin films were carried out using Philips X'pert pro X-ray diffractometer (GI-1°). Morphological studies of the films were carried out using SEM (Zeiss EVO-50, scanning electron microscope). EDS studies were carried out using the EDAX attached with the SEM. X-ray fluorescence spectroscopic studies were carried out to determine the elemental composition (using a Rigaku Model 3070E Rh-target wavelength-dispersive XRF spectrometer). The Raman analysis of CZTS thin film was carried out using Jobin Yvon T64000, triple monochromator Raman spectrometer. Excitation (514.5 nm) was provided by argon ionized laser. Optical properties were studied using UV-Vis spectrophotometer (Shimadzu UV-1800). Tecnai-G2 F-30, HRTEM was used for TEM studies. The electrical resistivity (ρ), carrier concentration and mobility were measured in the Van der Pauw configuration on 3 mm \times 3 mm sample. Electrical measurements from 77 K to room temperature were carried out to estimate the activation energy.

Three samples having different Cu, Zn, Sn, and S ratios were studied for their structural, morphological, and compositional properties. The details of the samples are presented in Table 2. The chemical compositions (determined using EDAX) are also presented in Table 2.

TABLE 2: Chemical composition and the ratio of different elements in the samples.

Sample	Chemical composition				Compositional ratio		
	Cu (at %)	Zn (at %)	Sn (at %)	S (at %)	Cu/(Zn + Sn)	Zn/Sn	S/metal
1	30.65	11.77	12.07	45.51	1.2856	0.9751	0.8352
2	28.99	11.77	13.82	46.03	1.1328	0.8516	0.8433
3	26.12	16.32	12.39	45.17	0.9097	1.3171	0.8258

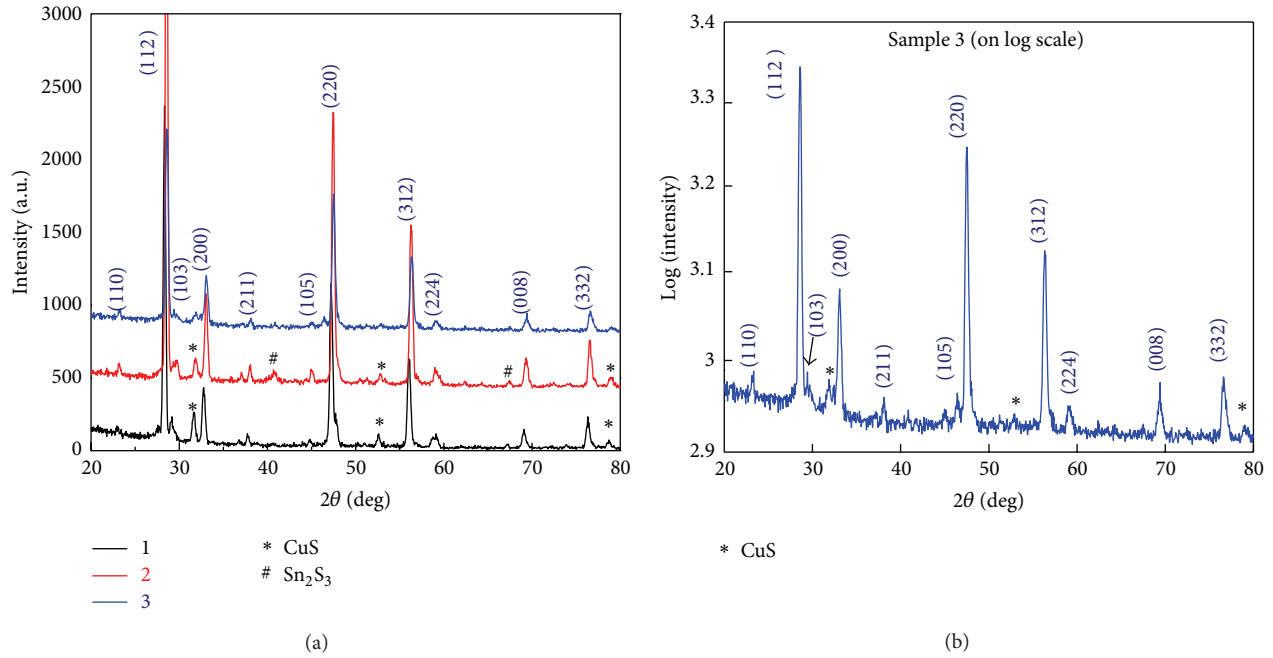


FIGURE 1: (a) GIXRD spectra of CZTS samples 1, 2, and 3 and (b) log scale plot of GIXRD of sample 3. Peaks corresponding to CZTS are shown, and peaks corresponding to CuS and Sn_2S_3 are marked as * and #, respectively.

3. Results and Discussions

Figure 1 shows the glancing incidence X-ray diffraction patterns of CZTS samples 1–3. In the GIXRD [19] pattern of all three films (usually for thin film samples, XRD is carried out in glancing incidence mode in order to remove/minimize substrate effect), peaks corresponding to kesterite CZTS structure were observed and are indexed as (110), (112), (103), (200), (211), (105), (220), (312), (224), (008), and (332) planes in Figure 1 [20]. The diffraction pattern of sample 1 (Figure 1(a)) shows two types of crystal structures, one corresponding to CZTS and the other corresponding to CuS (at $2\theta = 31.7$ (103), 52.6 (108), and 78.7 (213); JCPDS no. 78-239) and are marked as *. The composition of the film (determined using EDS analysis) is presented in Table 2. The Cu/(Zn + Sn) ratio of 1.28 and Zn/Sn ratio of 0.97 showed that the film was copper rich and zinc poor. SEM micrograph of CZTS films is shown in Figures 2(a)–2(c). These hexagonal crystallites are assumed to be CuS as shown in the SEM micrograph of sample 1 (Figure 2(a)).

In the GIXRD pattern of sample 2 (Figure 1(a)), main peaks belong to kesterite CZTS. Apart from these, peaks of other binary sulfides such as CuS (marked as *) (at $2\theta = 31.7$ (103), 52.6 (108), and 78.7 (213); JCPDS no. 78-2391)

and Sn_2S_3 (marked as #) (at $2\theta = 40.8$ (015) and 67.6 (325); JCPDF no. 75-2183) are also present. In the GIXRD spectrum of sample 2, the peaks corresponding to CuS were less intense compared to peaks in GIXRD pattern of sample 1. Compositional analysis (by EDS) shows Cu/(Zn + Sn) ratio of 1.13 and Zn/Sn ratio of 0.85. Thus, the film was copper, tin rich and zinc poor. In the SEM micrograph (Figure 2(b)), hexagonal shape is assumed to be of CuS crystallites, and cubical shape is assumed to be of Sn_2S_3 crystallites which can be seen.

In the GIXRD pattern of sample 3 (Figure 1(a)), all the main intense peaks are due to CZTS kesterite phase. The GIXRD pattern plotted on log scale has been shown in Figure 1(b). It appears that minute quantity of CuS phase may also be present in the sample. The small values of full width at half maximum (FWHM) indicated the crystalline nature of the film. SEM micrograph (Figure 2(c)) of film reveals that the film consisted of columnar grains of about 100 nm. EDS analysis showed Cu/(Zn + Sn) ratio of 0.91 and Zn/Sn ratio of 1.31. XRF spectroscopic studies were used to determine the atomic content of CZT and CZTS films (sample 3). For CZT film, the atomic percentages of Cu, Zn, and Sn were 52, 26, and 22%, respectively, and for CZTS film atomic percentage of Cu, Zn, Sn, and S were 21.3, 16.8, 12.4, and

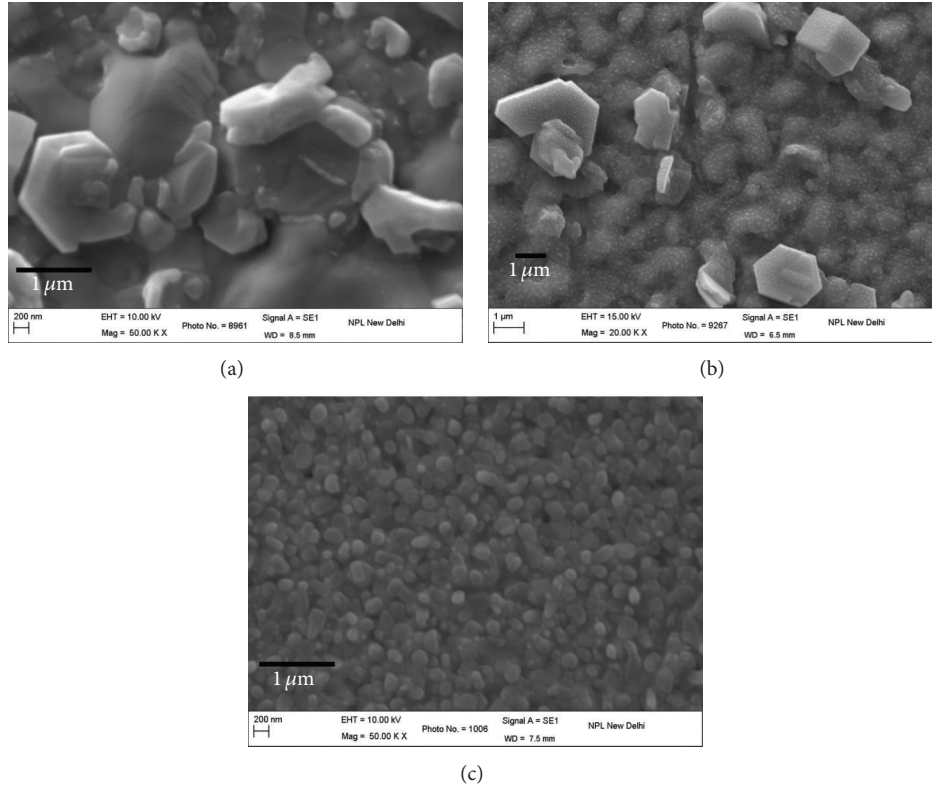


FIGURE 2: SEM micrograph of CZTS; (a) sample 1: few CuS crystallites are observed, (b) sample 2: some CuS and Sn₂S₃ crystallites are observed at the surface, and (c) sample S3: surface consists of columnar grains.

50.4%, respectively. This kind of columnar growth may be beneficial for decreasing the minority carrier recombination in CZTS solar cell device.

Sample 3 was further investigated using Raman spectroscopy, and the result is shown in Figure 3. The observed peaks at 332 and 285 cm⁻¹ in the Raman study are consistent with the Raman peaks of CZTS kesterite structure [21, 22]. Thus, GIXRD and Raman studies confirmed the kesterite CZTS structure of the film.

The optical absorption coefficients of the CZTS thin films in the energy range 1.1 eV–4.0 eV were studied. The absorption coefficient was larger than 10⁴ cm⁻¹ in the visible region, which is consistent with the reported literatures [1, 23–28]. The band gap for the direct band gap materials can be estimated using the following:

$$(\alpha h\nu)^2 = A(h\nu - E_g). \quad (1)$$

Based on the allowed direct interband transition, the band gap of film 3 was determined to be 1.50 ± 0.01 eV by extrapolating the linear (αhν)² versus hν plots to (αhν)² = 0, as shown in Figure 4. The value of band gap is in good agreement with the band gaps reported for CZTS films [1, 23–29]. This value is quite close to the theoretical optimal value reported for a single-junction solar cell.

The hot-probe measurement indicated that the CZTS thin film was p-type. The Hall effect measurement was carried out in a magnetic field intensity of 0.5 T and current

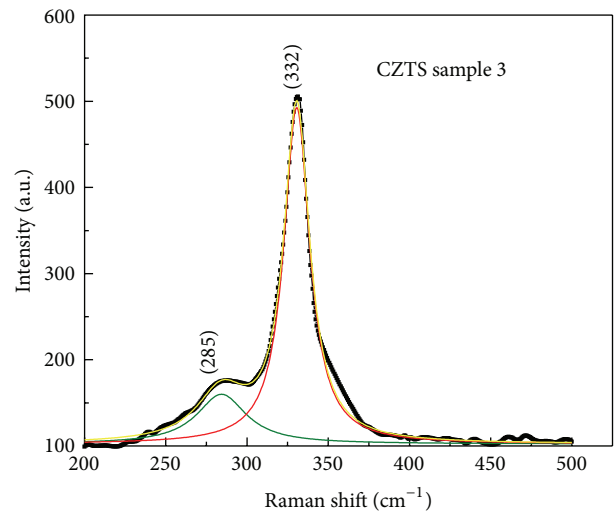


FIGURE 3: Raman spectrum of CZTS sample 3. Peaks at 285 and 332 correspond to CZTS.

flow of 1.0 mA. The values of the Hall coefficient, carrier concentration, resistivity, and mobility of the CZTS film 3 using the Van der Pauw geometry were 4.9 × 10² cm³C⁻¹, 1.25 × 10¹⁶ cm⁻³, 7.6 Ωcm, and 65 cm²V⁻¹s⁻¹, respectively. In one study, Zhou et al. have reported a value of 3.81 × 10¹⁸ cm⁻³ for carrier concentration and 12.61 cm²V⁻¹s⁻¹ for the Hall

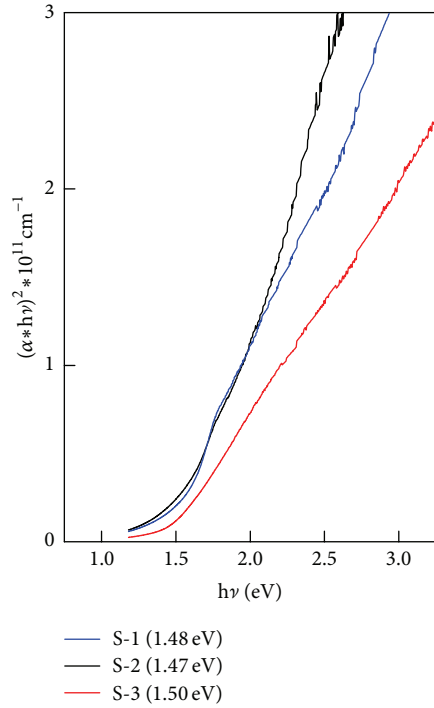


FIGURE 4: $(\alpha h\nu)^2$ versus photon energy ($h\nu$) plot for CZTS films 1, 2, and 3.

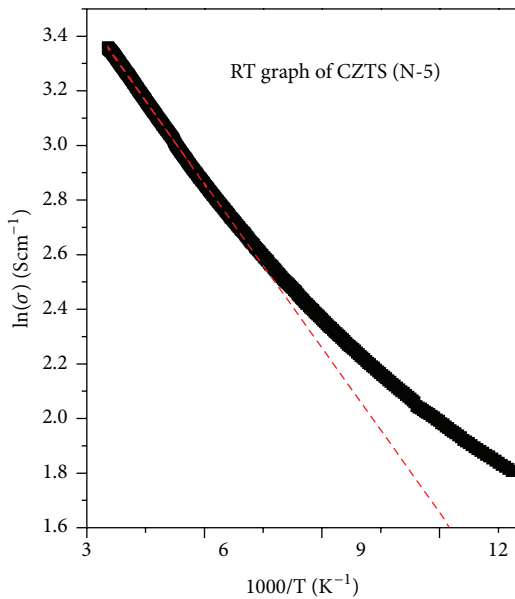


FIGURE 5: Temperature-dependent electrical conductivity for sample 3.

mobility in screen printed $\text{Cu}_2\text{ZnSnS}_4$ layers made on polyimide substrate. The screen printing paste was made from CZTS microparticles prepared by ball milling and sintering methods [30]. The positive value of the Hall coefficient confirmed the p-type nature of CZTS films. The obtained value of carrier concentration is similar to the values reported for device quality CIGS [31, 32] and also similar to the values

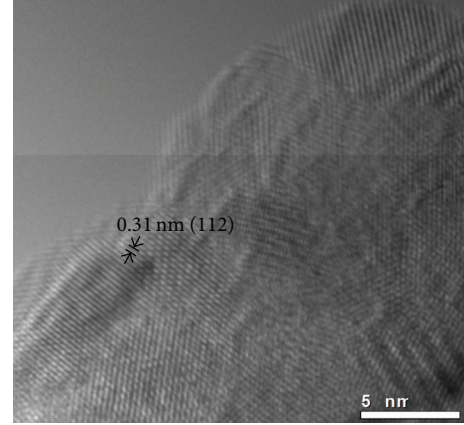


FIGURE 6: HRTEM micrographs of CZTS sample 3.

reported for CZTS by Liu et al. [1], Scragg et al. [29, 33], and Katagiri [34]. The resistivity value of thin film is similar to the results reported for CZTS film prepared by sulfurization of metallic precursors [1, 35] and spray pyrolysis method [26, 36]. The conductivity of the film was also measured in the temperature range of 77–300 K. Activation energy was calculated using the slope of the $\ln(\sigma)$ versus $1000/T$ (K) graph (Figure 5). The calculated value of $E_a \sim 35$ meV is similar to the value of $E_a \sim 29\text{--}40$ meV reported by Leitao et al. [37] and Gonzalez et al. [38]. With CZTS being a p-type semiconductor, this value of activation energy indicates that the mobility of free holes is almost independent of the temperature; that is, the free holes have enough energy to flow over the grain potential barriers.

Figure 6 shows the HRTEM micrograph of CZTS thin film sample 3. The lattice spacing of 0.31 nm corresponds to the (112) plane of kesterite CZTS. The different orientation shows the polycrystalline nature of the sample.

In short, it is to be noted that this is the first study on cosputtering from the metal targets and sulfurization in ambient H_2S . Using metal targets helps in controlling the composition of the film. It has been shown in the present study (with the help of GIXRD, SEM, and EDS) that various other sulfide phases are also formed depending upon the initial composition of metallic film. These sulfide phases may pose a problem in making the solar cell. The present study will provide a guideline for controlling the stoichiometry of CZTS films and avoiding the formation of secondary phases.

4. Conclusions

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films were grown on soda-lime glass substrates by cosputtering from individual metal targets and sulfurization in ambient H_2S for the first time and were characterized by Raman, XRD, SEM, EDS, XRF, HRTEM, optical transmittance (UV-Vis), the Hall measurements, and RT measurements. Films having CZTS phase with good crystallinity and strong preferentially oriented growth along (112) plane have been deposited. The values of the Hall coefficient, carrier concentration, resistivity, and mobility of the CZTS film were $4.9 \times 10^2 \text{ cm}^3 \text{ C}^{-1}$, $1.25 \times 10^{16} \text{ cm}^{-3}$,

7.6 Ωcm , and $65\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. The grown CZTS film demonstrated an optical absorption coefficient higher than 10^4 cm^{-1} and optical band gap of $1.50 \pm 0.01\text{ eV}$. The optical and electrical properties showed that the thin film is suitable for solar cell applications.

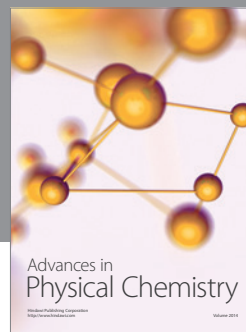
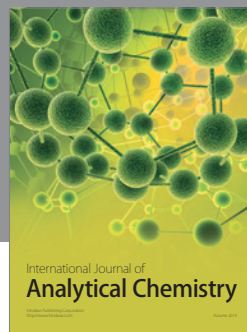
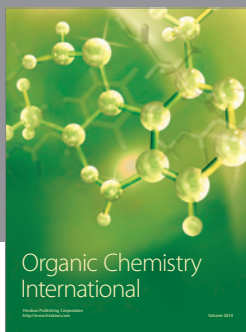
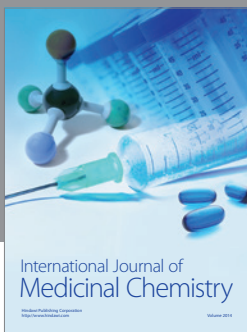
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