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Secondary Phases in CZTS Thin Films Grown Using Direct Liquid Coating Approach

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Abstract

The CZTS films are made by direct liquid coating of solution precursors. A benign solution of propanol and polyethylene glycol as solvent is used. Films of CZTS are prepared by drop casting and spin coating followed by annealing and sulfurisation. The present synthesis need as low as 350^oC to form the kesterite phase CZTS films. The presence of secondary phase in CZTS films are not conclusively detectable using X-ray diffraction and hence the role of Raman spectroscopy for the same is emphasized.

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1. Introduction

The quaternary kesterite phase Cu_2ZnSnS_4 CZTS has a band gap of 1.5eV and a high absorbing coefficient (>10^4cm^{-1}). In addition the constituent in CZTS are natural abundant making it a strong candidate for thin film solar cell absorber material. A facile ecofriendly solution processed direct liquid coating DLC approach for making CZTS thin film provides addition advantage of scalability, low energy input, easy processing steps and consequently low cost over other thin film growth techniques. Solution processed additionally provides an advantage of scalability, low energy input, and easy fabrication steps, low cost, over non vacuum techniques. Solution processed techniques provide easy accessibility for cation substitution to vary the composition and play with doping level of constituent $Cu_2Zn_xM_{(1-x)}Sn_yN_{(1-y)}S_4$ (where M & N are metal like Co,Ni,Fe,Mg; Ge,Ga,Si;) [1,2] and x, y ranges from 0 to 1. Anion ratio of sulphur and selenium and be adjusted in films by annealing in particular environment. Non vacuum processed CZTSSe solar cell with efficiency of 12.6% [3], and 11.2% [4] has dominated vacuum processed CZTS solar cell which has reported efficiency of 10.8% [5]. Research effort on complete non vacuum and solution processed CZTS solar cell [6-8] has achieved efficiency of 2.03% using methoxyethanol as solvent. Balled milled

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and screen printed CZTS shown efficiency of 0.6% [9]. Dimethyl sulfoxide (DMSO) a much celebrated solvent has achieved efficiency of upto 11% [4, 10-12] for fully solution processed CZTS based solar cell. Solvent used for solution processed CZTS include hydrazine (12.6%) [3], hexylamine (7.8%) [13], methanol, pyridine, ethylcellulose, DMF have associated environmental impact. The DLC based one step film preparation is an attractive prospect for solution processed solar cells, where phase formation happen upon annealing. However CZTS is a quaternary material which is relatively tough to synthesize in selective phase trivially without any secondary phases, figuring out a safer and stable solvent becomes an important step to be addressed for direct solution processed CZTS films. A detailed prospect of DLC is summed in review by T. Tedorov *et. al.*[14]. Here we report two solvent system (isopropanol and polyethylene glycol) as possible ecofriendly solution processed CZTS. The exploration of secondary phases is performed using X-ray diffraction and Raman spectroscopy. This molecular precursor is stable for over 1 month period. It's a continuation of our work in http://arxiv.org/abs/1510.05084.

2. Experimental details

Metal precursors $CuCl_2.2H_2O$, $ZnCl_2$, $SnCl_4.5H_2O$, and thiourea were used in ratio 1:0.75:0.5:3. For this Copper, Zinc and Tin salts are dissolved in isopropanol sequentially under stirring to obtain a greenish solution. Thiourea is dissolved in polyethylene glycol and stirred to form a second solution. Under stirring the isopropanol solution is added to the latter solution to form a transparent molecular precursor. Under vigorous stirring, an intermediate brown colour appeared for few seconds and then the solution turns transparent again. The final transparent solution is stored for drop casting/spin coating of CZTS films. Annealing is done at different temperature in open air. A custom designed setup is used for sulphurisation and selenisation. Film and sulphur are put in graphite crucible and are placed in a cup shaped heater for sulphurisation at different temperatures. The x-ray diffraction (XRD) of films is done using Rigaku TTRX-III XRD employing Cu K_α radiation. The Raman spectroscopy is performed using 532 nm excitation laser with a spot size of ~ 1μm and typical power of 200 μW. The optical study is performed using Perkin Elmer UV visible spectroscopy in wavelength range of 300nm to 1000nm.

3. Results and discussion

Figure 1 shows the XRD patterns for DLC coated CZTS films on borosilicate glass substrates which are annealed at various temperatures in the range 150-350°C. As we increase the annealing temperature, the precursor peak corresponding to SnS_2 gradually reduces and is found to be absent at an annealing temperature of 350°C. The CZTS XRD pattern is matched with JCPDS data card no-01-075-04122 which is also plotted as stick diagram for reference. Spin coated film of CZTS are prepared on a variety of substrates including normal borosilicate glass, ITO coated glass and sputtered gold substrate under identical growth conditions. Figure 2 summarizes the XRD data for the films grown on different substrates. The hallmark XRD peaks of CZTS were observed for films grown on all the substrates used in this study. The JCPDS data for CZTS is shown in Fig. 2(a). The substrate peaks are marked along with the corresponding JCPDS data in the panels (b) and (c) of Fig.2. As can be observed, it is very difficult to conclude the presence of any secondary phases using XRD alone.

The Raman spectra taken for the film grown on borosilicate glass is shown in the Fig.3 and a deconvolution of peaks is shown. The peak at 337 cm^{-1} [15,16] correspond to the A_1 vibrational symmetry mode of sulphur atom in CZTS. Broadening at the sides of peak at 305 and349 cm^{-1} are observed in the Raman spectra. Peak at 349 cm^{-1} corresponds to ZnS and that at 305 cm^{-1} to ternary Cu_2SnS_3 phase. These secondary phases have been found to be difficult to remove using a number of post annealing treatments. Our initial precursor ratio is Zn rich with a Zn/Sn ratio of 1.5 and Cu/(Zn+Sn) ratio of 0.8. The prepared films are having pure CZTS phase as it has single Raman shift peak as observed in Raman spectra.

Absorbtion spectra of film is shown in Fig.4. Absorption coefficient α was calculated to evaluate the optical band gap using $(\alpha h\upsilon)=A(h\upsilon-Eg)^n$ formula. Extrapolation to hυ axis of the Tauc plot of $(\alpha h\upsilon)^2$ vs hυ curve gives bandgap (eV) as shown in inset of Fig.4. In our sample the observed bandgap is 1.6eV. As the ratio of Cu/(Zn+Sn) decreases, the band gap has been reported to increase [17]. The Cu/(Zn+Sn) ratio is 0.8 in our case and hence the observed band gap is in agreement with published literature [17].

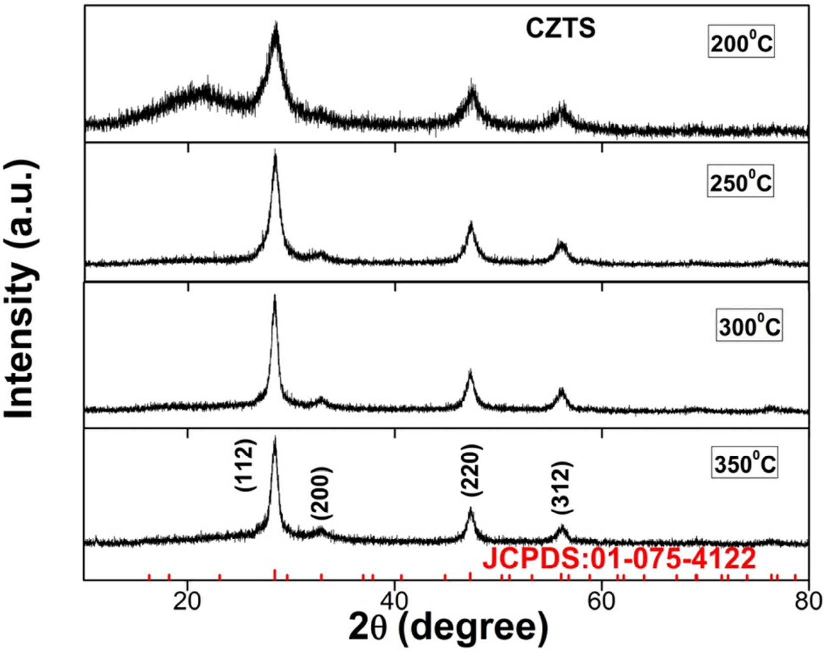

Figure 1 XRD data for films grown on borosilicate glass with different annealing temperatures in the range 150-350^{o}C.

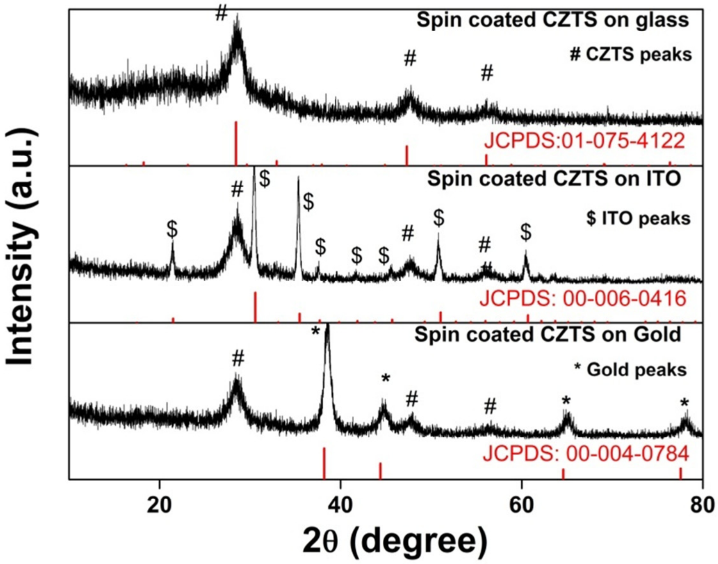

Figure 2 XRD data for CZTS films grown on borosilicate glass, ITO and sputtered gold substrates annealed at 350^{o}C.

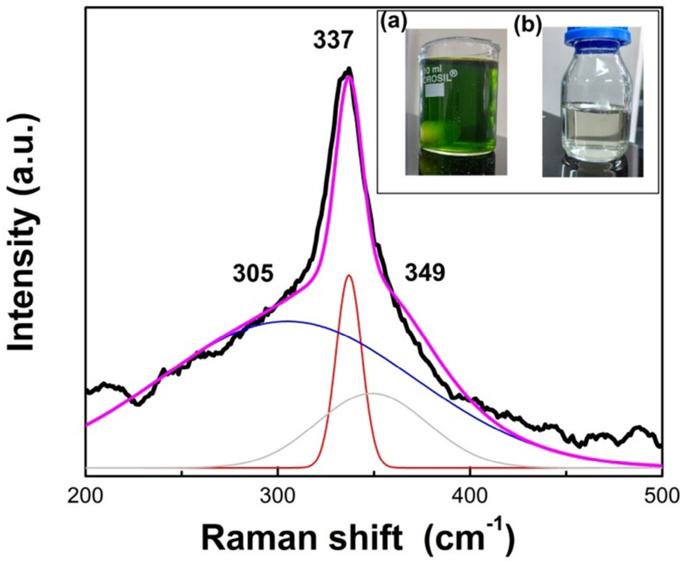

Figure 3 Raman spectra of CZTS film using 532 nm laser. Inset shows pictures of (a) Isopropanol solution and (b) final molecular precursor.

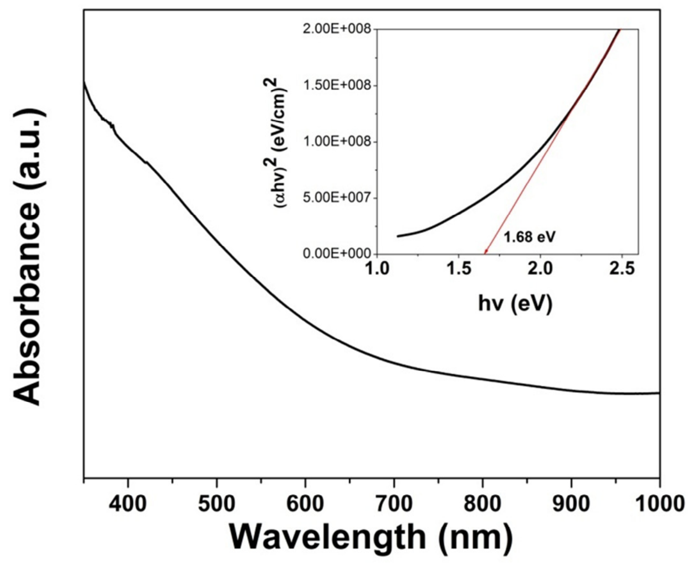

Figure 4 UV visible absorption spectra of CZTS film. The inset shows the Tauc plot for estimation of band gap.

4. Conclusion

Using Raman spectroscopy, the secondary phases of ZnS and Cu_2SnS_3 are found to be present in CZTS films. These are practically untraceable using XRD studies. The relative strength of the Raman peaks for the secondary phases are weak compared to that for CZTS. The grown film is observed to have a band gap of 1.68 eV which useful for photovoltaic applications however, the role of secondary phases in determining the open circuit voltage (V_{OC}) needs further investigation. The presented synthesis route using benign solvents and the one step film formation is scalable. Further work on solar cell device formation using these films is underway.

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