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A low-cost, sulfurization free approach to control optical and electronic properties of CZTS via precursor variation

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Abstract

Thin films of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) were synthesized via a low cost, wet chemical technique of chemical bath deposition (CBD). In the first part of this study, the chemical composition ratio $\text{S}/(\text{Cu}+\text{Zn}+\text{Sn})$ was varied keeping $\text{Cu}/(\text{Zn} + \text{Sn})$ and Zn/Sn ratios constant to study the effect of sulfur variation. Detailed electrical and optical characterization has been carried out using UV-Vis spectroscopy, x-ray diffraction, x-ray photoelectron spectroscopy, Raman spectroscopy and Kelvin probe force microscopy (KPFM) techniques. The results of the present study confirm that near ideal stoichiometry could be achieved in CZTS by adding excess thiourea in a controlled manner which eliminates the need for the normally used post-synthesis and high temperature sulfurization step. Using the stoichiometric sample as the basis, in the second part of the study $\text{Cu}/(\text{Zn}+\text{Sn})$ and Zn/Sn was varied and it was found that the electronic properties of CZTS in terms of band gap, work function and valence band edge position could be controlled by precursor variation. The Cu-poor, Zn-rich samples showed a better photoresponse which has been attributed to a decrease in the Cu_{Zn} type defects. The study thus demonstrates a scalable and low-cost technique to grow CZTS absorber layers for solar cells with control over its electronic properties which is important for effective device operation.

1. Introduction

Low cost, environmentally friendly and large scale photovoltaic energy generation requires a semiconductor absorber material having a high absorption coefficient, large carrier diffusion length, suitable band gap and good junction quality. Additionally, it should be abundantly available in nature and allow a reasonably low cost of synthesis. One of the top contenders in the search for an ideal PV absorber is $\text{Cu}_2\text{ZnSnS}_4$ or CZTS, a quaternary

semiconductor compound with a I₂-II-IV-VI₄ type structure with properties very similar to those of CIGS without being constituted of costly and rare earth elements [1,2].

CZTS films have been deposited using a number of physical and chemical means. Physical methods include thermal evaporation, sputtering and pulsed laser deposition [3-7]. However, these methods are expensive compared to simpler wet-chemical methods as they require the use of vacuum equipment [8]. Therefore, chemical based methods which include sol-gel synthesis, successive ionic layer adsorption and reaction (SILAR), chemical bath deposition (CBD), electrodeposition and nanocrystalline ink synthesis are quite promising [9-18]. In general, it is seen that sulfur loss is one of the most pressing issues that leads to the requirement of high-temperature sulphurization to obtain stoichiometric CZTS films [19-21]. At the same time, being a multi-element material, controlling the composition of CZTS is one of the most challenging tasks, and achieving this with purely wet-chemical based methods adds to the complexity. The effect of variation of Cu and Zn ratios has been investigated in spray pyrolyzed films and it is found that it was necessary to have both Cu-poor and Zn-rich conditions to obtain the best quality films with minimal unwanted secondary phases [22]. It has also been shown [23] that as the Cu/Zn ratio increases, the hole density increases which was attributed to formation of Cu_{Zn} type acceptor defects. The effect of Cu precursor variation in sol-gel synthesized films showed that as Cu/(Zn+Sn) decreased, grain size increased and the band gap shifted to higher energies [24]. Another study on sol-gel synthesized CZTS reported that with an increasing amount of S or Cu (keeping the other metals constant), the thickness of the film increased, while increasing S and decreasing Cu caused a blue shift in the band gap [25].

To the best of our knowledge, there isn't any study which demonstrates the change in electrical and optical properties with varying precursor ratios of CZTS films synthesized by chemical bath deposition. To be able to successfully use this semiconductor material for large scale solar cell synthesis, a detailed study of the dependence of structural, optical and electronic properties of CZTS films as a function of composition is of key importance. In addition, it has been seen that there are very few studies which have demonstrated the use of scanning probe techniques to qualitatively evaluate the CZTS absorber layer. Most commonly, KPFM has been used to correlate grain boundary potentials with film quality. KPFM done on reactively co-sputtered films of CZTS and CZTSSe clearly demonstrated that there exists a higher, positive surface potential at the grain boundaries and this finding was correlated with conducting AFM data showing a higher current in these same regions [26]; another study on CZTS films grown by the same method showed using conducting AFM and KPFM that the photocurrent primarily flowed along grain boundaries and capacitance microscopy [27] was used to show that the charge separation takes place at the interface of the grain boundary and grain and the current predominantly moved along these boundaries [28,29]. KPFM has also been used to detect the presence of unwanted secondary phases on the surface of CZTS films by KCN-etching [30] as well as in CZTSSe by depth profiling [31].

As can be seen, almost every study is based on sputtered films with no correlation made between stoichiometry and measured surface potential. Thus, the aim of the present study was three-fold, firstly, a simple wet-chemical technique has been used to obtain stoichiometric CZTS films without the need of the additional high-temperature sulphurization step. In the second part of the study, the effect of precursor variation (by varying copper and zinc quantities) was examined on the structural, optical and electronic properties of the material. Finally Kelvin probe force microscopy has been used as a quantitative and qualitative measure of the quality of the CZTS films as absorber materials by measuring the improvement in photoresponse as Cu and Zn quantities change. This technique would provide a unique, non-destructive method of evaluating film quality without the need of depositing the successive layers and completing the device.

2. Experimental details

Synthesis of CZTS films was carried out using chemical bath deposition on glass and indium-tin-oxide (ITO) coated glass substrates. Prior to deposition, the substrates were cleaned by sonicating in a mild laboratory detergent in de-ionized water followed by propanol and finally acetone to remove inorganic and organic impurities. The precursors used for synthesis were copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$), zinc acetate ($\text{Zn}(\text{CH}_3\text{CO}_2)_2$), stannous chloride (SnCl_2) and thiourea ($\text{CH}_4\text{N}_2\text{S}$) with methanol (CH_3OH ; HPLC grade) as the solvent. All of there were purchased from Merck chemicals and were at-least, or greater that 99% purity. Seven samples (S1, S2, S3 with sulfur variation and S4 – S7 with Cu and Zn variation) were prepared in 50 ml of methanol each. The molarities of each of the precursors for the samples were chosen according to the following table

Sample Name	Elemental ratios
S1	$\text{Cu}/(\text{Zn}+\text{Sn}) = 1$; $\text{Zn}/\text{Sn} = 1$; $\text{S} = 4$
S2	$\text{Cu}/(\text{Zn}+\text{Sn}) = 1$; $\text{Zn}/\text{Sn} = 1$; $\text{S} = 8$
S3	$\text{Cu}/(\text{Zn}+\text{Sn}) = 1$; $\text{Zn}/\text{Sn} = 1$; $\text{S} = 20$
S4 (Cu rich, Zn poor)	$\text{Cu}/(\text{Zn}+\text{Sn}) = 2$; $\text{Zn}/\text{Sn} = 0.9$; $\text{S} = 20$
S5 (Cu poor, Zn rich)	$\text{Cu}/(\text{Zn}+\text{Sn}) = 0.9$; $\text{Zn}/\text{Sn} = 1.1$; $\text{S} = 20$
S6 (Cu poor, Zn rich)	$\text{Cu}/(\text{Zn}+\text{Sn}) = 0.8$; $\text{Zn}/\text{Sn} = 1.2$; $\text{S} = 20$
S7 (Cu poor, Zn rich)	$\text{Cu}/(\text{Zn}+\text{Sn}) = 0.7$; $\text{Zn}/\text{Sn} = 1.3$; $\text{S} = 20$

Table 1. Precursor ratios for samples S1 to S7

Separate beakers were used for carrying out the reactions simultaneously. After the precursors had been weighed and added to their respective beakers, 50 ml of methanol was added to each and the solutions were allowed to stir until all the salts had dissolved completely. Following this, the substrates were dipped into the solution by submerging them completely for 30 seconds and then taken out and placed on a clean petri dish. After the first round of dipping, the sample was heated at 250°C in an oven for 25 minutes. A thin black film was formed on the substrates indicating the formation of the first layer of CZTS however the film was non-uniform. Therefore, the cycle of dipping and heating was repeated two times more until a uniform, black film of CZTS was formed. Finally a separate annealing was carried out at 350°C (in air on a hot plate) to ensure a well-formed, homogenous film. After this the samples were stored for further analysis.

3. Results and discussion

3.1 Sulfur variation (samples S1-S3):

To obtain the ratio of the elements present in the films grown with different precursor ratios, EDX analysis was carried out. As the molarity of the sulfur precursor was increased, the ratio S/(Cu+Zn+Sn) increased from 0.7 to 1.1 (from S1 to S3). Thus sample S3 is the closest to the correct stoichiometry even without the external sulfurization step. X-ray diffraction was carried out to confirm the formation of the CZTS phase and the resulting patterns are shown in figure 1. The spectra show the characteristic peaks for kesterite CZTS (JCPDS card no. 260575) with 2θ values of 28.5°, 37.73°, 47.3° and 56.16°. However samples S1 and S2 have many secondary phases also present with XRD peaks corresponding to SnS (21.5° and 51.11°), CuS (31.1°, 35.4° and 60.64°), Cu₂S (45.68°) and SnS₂ (41.91°, 62.26°). As the sulfur content is increased, the formation of the secondary phases decreases and sample S3 shows peaks corresponding only to kesterite CZTS (112), (220) and (312) planes and no discernable peaks for other secondary phases. However, it is well known that due to the overlap of the diffraction pattern of the ZnS secondary phase with CZTS, XRD alone cannot confirm the formation of single phase kesterite. Therefore, Raman spectroscopy was carried out on the samples and the results are shown in figure 2. The spectra has been deconvoluted to gain a better understanding of the different phases present in the material and changes in their relative intensity with changes in the precursor ratio. The peaks at ~334 cm⁻¹ and ~287 cm⁻¹ are the primary and secondary characteristic peaks for kesterite CZTS phase respectively [32-34]. The peaks at ~358 cm⁻¹ and ~657 cm⁻¹ can be attributed to ZnS [33,35] while the peak at ~471 cm⁻¹ belongs to Cu_{2-x}S [33], both of which are unwanted secondary phases. As the quantity of the sulfur precursor is increased, the intensity of the peaks indicating kesterite CZTS phase increase while those for the secondary phases of ZnS and Cu_{2-x}S decrease. Thus, both Raman analysis and x-ray diffraction data clearly confirm the formation of kesterite CZTS phase. The removal of unwanted phases with the presence of excess sulfur precursor may be explained by the fact that as thiourea content increases the availability of free sulfur increases. This in turn increases the number of metal-sulfur complexes associated with

free sulfur which directly leads to an increase in the available CZTS nucleation sites. Such a correlation has previously been observed in CZTS nanocrystals grown using thiourea as the sulfur source [36].

UV-Vis spectroscopy measurements on S1 and S2 showed the onset of absorption to be at ~2.2 eV and 2 eV respectively. This overall higher band edge position may be attributed to the significant presence of high band gap secondary phases such as ZnS, SnS₂ and CuS (as also indicated by XRD and Raman analysis). However for sample S3 the onset of absorption is at ~1.58 eV which corresponds well with the range of values reported in the literature for kesterite CZTS [37,38]. This decrease in band gap with increasing sulfur content has been previously reported in CZTS films where it was considered to be indicative of the removal of secondary phases. However it is important to note that in these earlier studies it was done with increasing sulfurization time [39] whereas in the present case it has been achieved by increasing the sulfur precursor concentration in the starting chemical bath solution without applying any post-synthesis processing. Thus it is inferred that samples S1 and S2 are not fully formed kesterite CZTS rather they are a mixture of secondary phases, however sample S3 can be called kesterite CZTS with almost negligible quantities of these unwanted phases.

To confirm the valence states of the elements present in the CZTS structure, high-resolution x-ray photoelectron spectroscopy (XPS) was performed on the samples. A standard ultra-high vacuum (UHV) chamber was used operating at a base pressure of less than 2×10^{-10} mbar with hydrogen as the main residual gas. The core-level electronic structure and occupied density of states in the valence band were probed by XPS using a SPECS monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV) operating at 200 W, together with a PSP Vacuum Technology electron-energy analyser operating with a constant pass energy of 10 eV. Calibration of the spectrometer was performed using a polycrystalline silver foil, cleaned in-vacuo. The Ag 3d_{5/2} photoelectron line had a binding energy (BE) of 368.3 eV and a full-width at half-maximum (FWHM) of 0.6 eV. The Fermi edge of the silver sample had a spectral width of 0.3 eV. From this calibration, tolerances were determined to be ± 0.1 eV for core-level binding energies and ± 0.05 eV for the valence band maxima (VBM). High-resolution spectra of the Cu 2p, Zn 2p, Sn 3d and S 2p regions were recorded and fitted using Voigt functions after a Shirley background had been subtracted. The XPS measurements were carried out after argon ion sputtering for five minutes to remove contaminants present in the top layers of the sample. Survey scans before and after sputtering showed that oxygen and carbon contamination is greatly reduced after this etching treatment. Binding energy values were calculated using the C 1s peak at 284.8 eV as the reference. The XPS spectra of S1, S2 and S3 are shown in figure 3. Part (a) shows the 2p_{1/2} and 2p_{3/2} doublet peaks for Cu. Two strong peaks appear at ~932.5 and 952.6 eV with a constant difference of ~19.8 eV which match the standard values for 2p_{1/2} and 2p_{3/2} for the Cu⁺ state. It's also seen that there is no shoulder peak at 933.7 eV which would have shown the presence of CuO with a Cu²⁺ valency. Moreover, shake-up satellite peaks that appear around 940 to 945 eV for CuO are also not observed. Figure 3 (b) shows the spectra for Zn in S1, S2 and S3. Two clear peaks at ~1022.1 and 1044.6 with a constant separation of

~22.5 eV match well with the standard values for Zn 2p_{3/2} and 2p_{1/2}. These peaks show the presence of Zn²⁺ in the material. The peaks at ~485.8 and 494.3 eV with a constant separation of ~8.4 eV match well with the Sn 3d_{5/2} and 3d_{3/2} states which indicate the presence of Sn⁴⁺. In addition to these, all the three samples show the Zn LMM Auger peaks at ~496.5 eV binding energy on the high energy side of the 3d spectrum for Sn. The S peaks for the three samples has been analyzed in detail by deconvoluting it to gain a better understanding of the species of sulfur present. Figure 3 parts (d), (e) and (f) show the XPS data for sulfur for samples S1, S2 and S3 respectively. It is seen that in all three cases, two distinct species of sulfur are present which have been marked in the plots. Species 1 has a lower set of binding energies (with S 2p_{3/2} peaks in the range of ~161.3 eV and S 2p_{1/2} peaks at ~162.5 eV) as compared to species 2 (with S 2p_{3/2} peaks in the range of ~162.5 eV and S 2p_{1/2} peaks at ~163.7 eV). As the quantity of sulfur is increased, the relative intensity of species 2 increases with respect to species 1 within each sample. This can be explained on the basis of the fact that each of these two species indicates sulfur bonding in a unique manner. Species 1 is due to sulfur bonded into the CZTS lattice and matches well with previously reported binding energy values and verifies the presence of the S²⁻ valence state. Species 2 has been ascribed to the unreacted thiourea present in the material and the relatively higher value of binding energy for the S 2p_{3/2} peaks at ~162.3 eV (for the =S in C(NH)₂S) match with the values reported for thiourea [40,41]. In addition it was observed that in all three samples, even after argon ion sputtering, the signal for nitrogen persists and its intensity increases from S1 to S3. All these observations correspond well with the fact that the intensity of species 2 is the highest in S3 because this sample had the maximum amount of excess thiourea added to it.

In addition to studying the crystal structure, band gap and valence states, the variation in the position of the Fermi level was also studied by two different techniques. The work functions of the three samples were determined from Kelvin probe force microscopy (KPFM). It was observed that as the quantity of sulfur increases in the samples, the work function correspondingly becomes larger or it can be said that the material becomes more p-type in nature. To further verify this, valence band measurements were carried out, the results of which also clearly showed that an increase in sulfur from S1 to S3 causes the Fermi level to move down towards the valence band edge or it can be said that the valence band maximum has decreased which can be attributed to the formation of holes in the material which would again correspond to an increase in the p-type nature of the film. This phenomena of an increase in the quantity of holes with an increasing amount of sulfur can be explained by the fact that as the number of competing secondary phases decrease from S1 to S3 (as seen by XRD and Raman analysis), the quality of the material improves and it takes on the inherent nature of CZTS which is p-type largely due to the presence of Cu_{Zn} type defects. It has also been previously reported that a decreased amount of free sulfur during CZTS synthesis is responsible for a decreased CZTS-like character and as the quantity of sulfur increases (in the present study by addition of excess thiourea), the material naturally becomes slightly Cu rich and Zn poor thus further encouraging the formation of the Cu_{Zn} acceptor-type defect.

The schematic diagram in figure 4 depicts the changes observed in the band structure of the material as the sulfur precursor is increased from sample S1 to S3. It can be seen that as sulfur incorporation increases, the band gap decreases, work function increases and the Fermi level moves closer to the valence band maxima. Thus sample S3 has stoichiometry closest to that required the ideal for CZTS. The above results show that the electrical and optical properties of CZTS can be controlled via a simple wet-chemical process and good stoichiometry can be achieved without the need of an additional high-temperature sulfurization step.

3.2 Cu and Zn variation (samples S4-S7):

Studies have shown that a Cu-poor and Zn-rich phase is desired in CZTS so that formation of Cu_{Zn} antisites is inhibited along with phases such as like Cu_2SnS_3 which are formed with Zn-poor conditions. However, with compositions that are Zn-rich, a competitive phase such as ZnS can be easily formed and this must be tried to be kept at a minimum. Therefore it is necessary to find the optimal Cu to Zn ratios for best device performance which was the aim of this part of the study. The difference in the present case from previous studies is that KPFM has been used as a tool to qualitatively and quantitatively evaluate the improvement in photoresponse of the films with changing Cu and Zn ratios.

In the previous section detailed studies carried out show that sample S3 has a stoichiometry consistent with kesterite CZTS when the ratios $\text{Cu}/(\text{Zn}+\text{Sn}) = 1$, $\text{Zn}/\text{Sn} = 1$ and $\text{S} = 20$ were used for precursor molarities during synthesis. Considering this sample as stoichiometrically correct CZTS, the current section details the study in which Cu and Zn ratios were varied while keeping Sn and S constant (as in the content used in S3). Specifically, the two ratios of $(\text{Cu}/\text{Zn} + \text{Sn})$ and (Zn/Sn) were varied with the aim of mapping the resulting change in the material's band structure. Four samples denoted by S4, S5, S6 and S7 were prepared and their precursor ratios are given in table 1. Since it is well known that a Cu-poor, Zn-rich composition is the best from the point of view of application to devices for CZTS [42,43], it was decided to keep one sample Cu-rich and the other three Cu-poor and Zn-rich. X-ray diffraction was carried out first to study the phase purity of the samples. Figure 5 parts (a), (b), (c) and (d) show the x-ray diffractograms for S4, S5, S6 and S7 respectively. For sample S4, in addition to the standard peaks for Kesterite CZTS at 28.4° , 47.6° and 56.0° there are a number of secondary peaks in the scan. These include Cu_2S (45.6°), CuS (31.1° , 35.4° and 60.7°), SnS (21.5° and 51.1°) and SnS_2 (41.91° , 62.26°).

Amongst these, the phases arising due to copper are the most prominent and this is expected as S4 is the Cu-rich sample. In S5 which is the first Cu-poor and Zn-rich sample, there is a drastic fall in the intensity of the secondary phases. Low intensity peaks are visible is CuS at 31.1° and 35.4° and SnS with a very small peak at 51.1° . In S6 and S7 which are progressively even more Cu-poor and Zn-rich, all the secondary 'spurious' phases disappear completely leaving only the three previously mentioned peaks belonging to CZTS.

Results of Raman spectroscopy are shown in figure 6. All the samples show that the A1 mode peak for CZTS is present at 332 cm⁻¹ as well as a small peak at ~474 cm⁻¹ which indicates the presence of CuS. However it can be seen that as the samples transition from Cu-rich to Cu-poor, the CuS peak becomes very small and additionally, a shoulder peak at ~287 cm⁻¹ can be seen to be becoming stronger which also corresponds to Kesterite CZTS. Therefore the data from Raman spectroscopy corroborates the conclusions we had drawn from the XRD scans.

Band edge measurements were carried out by UV-Visible spectroscopy and the data is shown in figure 7. For sample S4 it can be seen that there is an approximate absorption edge at ~ 1.5eV with a slight sub-bandgap absorption attributed to defect levels or secondary phases such as SnS and Cu₂S which have been shown previously to exhibit a second zone of absorption in the absorbance data for CZTS films. Now as the samples move towards becoming Cu-poor and Zn-rich it is seen that the sub-bandgap absorption disappears and a clear upward shift in the band edge positions are visible with sample S7 showing a value of ~1.67 eV. Thus, there is a trend of increasing band gap energy as the samples become progressively Cu-poor. The phenomenon of band-gap shrinkage with an increasing Cu/Sn ratio (or band gap increase with a decreasing Cu/Sn ratio) has been previously studied [44] and a number of theories proposed such as (i) bandgap variation because of stannite-Kesterite polymorphic transformations; (ii) the existence of solid solutions between CZTS and its secondary phases such as SnS or SnS₂ and (iii) shrinkage due to a large concentration of acceptor defects which reduces the bandgap by the formation of an 'acceptor band' near the valence band of the material. In the present case the sample S4 may have a similar acceptor band near its valence band edge due to the fact that it is Cu-rich and Zn-poor which can give rise to Cu_{Zn} type defect states that act as acceptors leading to an overall smaller bandgap and vice-versa in the case of S5, S6 and S7 which are increasingly Cu-poor.

Valence states of the different elements in the samples were determined by XPS analysis. As explained in the previous section for samples S1-S3, the C 1s peak at 284.6 eV was used as the reference and core-level binding energies were obtained by applying a least-square fitting procedure to XPS data after the Shirley background had been subtracted. Voigt lineshapes were used for the fitting. The peaks in figure 8 (a) at 932.1 eV and 951.8 eV with a separation of 19.7 eV correspond well with Cu 2p 3/2 and 2p 1/2 and are indicative of the formation of Cu⁺¹. Similarly in figure 8 (b), the peaks at 1021.3 eV and 1044.5 eV correspond to the Zn 2p 3/2 and 2p 1/2 doublet and show a separation of 23.2 eV confirming Zn to be in its Zn²⁺ state. Figure 8 part (c) shows that Sn is present in its Sn⁴⁺ state with peaks at ~484.8 eV and 493.1 eV with a separation of 8.3 eV in the form of the Sn 3d 5/2 and 3d 3/2 peaks. Finally, the peaks marked as S' in figure 8 parts (d), (e), (f) and (g) confirm the presence of the sulphide S²⁻ valence state with 2p 3/2 and 2p 1/2 peaks at ~161.6 eV and 162.7 eV with a peak separation of 1.1 eV. As in the case of samples S1 to S3, a second set of peaks have also been fit which (denoted by S'') which have been attributed to the unreacted sulfur in the form of thiourea. In addition, it can be clearly seen that as the samples become Cu-poor and Zn-rich, the intensity of the Cu 2p doublet peaks decreases and those of the Zn 2p doublet increases.

There is a small difference in the peak positions in case of Sn (~1.3 eV) between S4 and S7 however, the binding energies corresponding to these values still lie in the interval reported for Sn⁴⁺. Thus all the valence states of the samples are consistent with those of kesterite CZTS phase. In addition to the analysis of the binding energy values, the change in the two sulfur ratios (sulfur that has bonded within the CZTS structure and unreacted thiourea) as ratios of the areas of the fitted peaks was calculated and the data is shown in table 2. Here, S' is the area of the peaks corresponding to reacted sulfur which was 'species 1' in the last section and S'' corresponds to unreacted sulfur which was 'species 2' previously. The data shows that the ratio S'/S'' increases from S4 to S7. From this it is inferred that the Cu-poor and Zn-rich growth condition promotes the incorporation of sulfur into the crystal structure of the film.

Sample Name	S' (reacted)		S'' (unreacted)		Ratios	
	Area 1	Area 2	Area 1	Area 2	(S'1 + S'2) / (S''1 + S''2)	S'/S''
S4	305.0	152.5	155	77.5	457.5/232.5	1.96
S5	584.9	292.4	253.5	126.7	877.3/380.2	2.30
S6	356.4	178.2	148.8	74.4	534.6/223.2	2.39
S7	337.2	168.6	122.2	61.1	505.8/183.3	2.75

Table 2. Ratios of reacted to unreacted sulfur for samples S4 to S7

Surface potential measurements and corresponding work function calculations on the films were done using KPFM technique and the results are shown in figure 9 (a). The plot clearly shows that as the samples go from being Cu-rich Zn-poor to Cu-poor Zn-rich, the work function values fall consistently. Samples S4 - S7 show a work function of 5.47, 5.42, 5.36 and 5.15 eV, respectively. Thus it can be seen that unlike the results from the samples with the varying sulphur content, the change in Cu and Zn ratio causes large changes in the work function with a difference of almost 320 mV between S4 and S7. From this trend it can be inferred that as Cu decreases and Zn increases in the samples, the Fermi level of the semiconductor shifts up thereby indicating a decreased p-type behaviour from samples S4 to S7. Valence band offset measurements were performed on these samples and the results are shown in figure 9 parts (b - e). As one moves from sample S4 to S7, the separation of the valence band edge from the Fermi level increases. The Fermi level is observed to be shifted by 0.14 eV, 0.34 eV, 0.4 eV and 0.49 eV from the valence band maxima for S7, S5, S6 and S7, respectively. Thus the results of the KPFM measurement and valence band offset measurements both prove the same point that removal of copper and introduction of excess zinc causes a decrease in work function and a shift in the Fermi level away from the valence band edge.

Surface potential (SP) measurements in the dark and then under illumination were also carried out and the average surface potential distribution is obtained from these images and plotted in the form of histograms. The difference between dark and light surface potentials is a measure of the photoresponse of a particular sample. Figure 10 (a), (b), (c) and (d) show the surface potential histograms in the dark and light for samples S4 to S7 respectively while

parts (e), (f), (g) and (h) show the 3D AFM topography images of the same samples. For sample S4, there is a negligible shift in SP as it goes from dark to light and this shift is of the order of ~ 3 mV. For sample S5, the photoresponse in terms of decrease in SP as it goes from dark to light only improves slightly (~ 8 mV). However in the case of S6 and S7 there is an appreciable difference in SP in the light of ~ 34 mV and 54 mV respectively. The final band diagrams of the samples with Cu and Zn variation are shown in figure 11 along with the trends observed in their optical and electrical properties.

It has been previously shown through extensive theoretical simulations as well as many experimental studies that it is the presence of Cu_{Zn} type antisite defects and V_{Cu} (copper vacancies) which primarily give rise to the inherent p-type nature of CZTS [45,46]. These defects have been shown to not change the overall electronic structure of CZTS but place the Fermi energy at the valence band maxima thus leading to the formation of a large number of shallow hole states [47]. Even between these two defect types, Cu_{Zn} has a lower energy of formation (0.01eV) as compared to V_{Cu} (0.57eV) therefore it is predicted that Cu_{Zn} is the dominant acceptor defect in CZTS grown under equilibrium conditions [45]. However, it has also been shown that the $(0/-)$ i.e. acceptor transition energy for Cu_{Zn} is 0.10eV above the VBM while for V_{Cu} the same value is 0.02eV . This makes the Cu_{Zn} level a deep defect state which can be detrimental to the performance of the material as an absorber layer in a photovoltaic device by causing a lowering in the open circuit voltage. It is to suppress the formation of these deep level defects that Cu-poor, Zn-rich conditions are preferred for synthesis of CZTS.

Based on the above, in the present study as we go from sample S4 to S7, the quantity of Cu decreases and that of Zn increases. The aim was to be able to decrease the number of Cu_{Zn} type antisite defects so as to improve the photoresponse of the material. These deep level defects would have acted as traps for photogenerated carriers thereby leading to a poor photoresponse (as seen in S4 which is extremely Cu-rich). The results of the characterizations carried out show that there is indeed a decrease in the work function accompanied by a drastic improvement in the photoresponse of the film as the material is made Cu-poor and Zn-rich which we can attribute to a sharp fall in the number of Cu_{Zn} type defects.

Conclusion.

The present study demonstrates that changing the precursor composition in the chemical bath allows: (i) the growth of stoichiometric CZTS by the use of excess thiourea in a controlled manner and (ii) the ability to manipulate the band structure of CZTS in terms of band gap, work function and valence band edge position by controlling $\text{Cu}/(\text{Zn}+\text{Sn})$ and Zn/Sn ratios.

On varying the sulfur content, the XPS results clearly show that sulfur is present in the form of two different species of unreacted sulfur (corresponding to thiourea) and sulfur (from the CZTS phase) especially in samples with a large amount of excess sulfur precursor. Increase in sulfur content results in arresting the growth of

secondary phases and phase pure CZTS films are grown without any post-synthesis sulfurization step. It is also shown that Cu-poor and Zn-rich growth conditions result in CZTS films with a negligible quantity of secondary phases and lead to increasing band gaps and decreasing work functions which have been attributed to a fall in the deep level Cu_{Zn} type defects which would otherwise have trapped photogenerated carriers and degraded the device performance. These results are further confirmed by an enhancement in the photoresponse of the film which is shown by the larger difference between dark and light surface potential values. The control demonstrated in this study over the optical and electronic properties by varying the initial precursor composition is extremely useful for the fabrication of solar cell devices. This is an important step towards the development of low-cost absorber materials which do not require the additional step of sulfurization allowing not only faster and simpler fabrication of these films on a large scale but also making the process economically viable. In addition, the ability to tune the band structure opens up many new avenues for other applications such as in photocatalysis, sensing and water splitting all of which require the material to have certain specific material properties. The technique demonstrated here allows control over these thus allowing the diverse use of this non-toxic, earth abundant material.

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Figures

Figure 1. X-ray diffraction data for samples (a) S1, (b) S2 and (c) S3.

Figure 2. Observed peaks of Raman spectra for samples S1, S2 and S3. Deconvolution has been carried out to analyze the presence of different phases.

Figure 3. XPS spectra for the S1, S2 & S3 samples with (a) Cu 2p_{3/2} and 2p_{1/2}; (b) Zn 2p_{3/2} and 2p_{1/2} and (c) Sn 3d_{5/2} and 2d_{3/2} with the Zn L2M45M45 auger peak at ~496.5 eV. Parts (d), (e) and (f) show the S 2p_{3/2} and 2p_{1/2} spectra for the two different species of sulfur present in samples S1, S2 and S3 respectively.

Figure 4. Energy diagrams of CZTS samples S1, S2 and S3 derived from the results of the present study. It can be seen that as thiourea content increases, band gap decreases, work function increases and valence band maxima decreases.

Figure 5. X-ray diffraction data for samples (a) S4, (b) S5, (c) S6 and (d) S7

Figure 6. Raman spectra for samples S4 to S7 with the CZTS characteristic peak at 333 cm^{-1} observed in all the samples

Figure 7. Absorbance data showing progressing increase in band-edge position from S4 to S7

Figure 8. XPS analysis of S4 to S7 showing peaks for: (a) Cu 2p $3/2$ and 2p $1/2$; (b) Zn 2p $3/2$ and 2p $1/2$; (c) Sn 3d $5/2$ and 3d $3/2$ (and an Auger peak) and (d), (e), (f), (g) for S 2p $3/2$ and 2p $1/2$. The fitted peaks corresponding to reacted (S') and unreacted (S'') sulfur have been labelled.

Figure 9. (a) Work function variation for S4 to S7; parts (b), (c), (d) and (e) show valence band offset measurements for S4 to S7

Figure 10. Parts (a) to (d): 3D topography scans of samples S4 to S7; parts (e) to (h) show shifts in average surface potential for S4 to S7 when samples are taken from dark to light

Figure 11. Band structure mapping of samples S4, S5, S6 and S7 based on the results of this study (CBM = conduction band minimum, VBM = valence band maximum, FL = Fermi level, WF = work function, Eg = bandgap energy)