Electrochemical Synthesis and Characterization of Cu$_2$ZnSnS$_4$ Thin Films

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**Abstract**

Cu$_2$ZnSnS$_4$ (CZTS) thin films have been electrochemically deposited from aqueous electrolyte containing CuCl$_2$, ZnCl$_2$, SnCl$_4$ and Na$_2$S$_2$O$_3$ onto fluorine doped tin oxide (FTO) coated glass substrates. A conventional three-electrode geometry consisting working, counter and reference electrodes was used to perform the electrochemical experiments. The films were deposited at -1.1 V with respect to Ag/AgCl reference, which was optimized by cyclic voltammetry. CZTS layers were annealed in tube furnace at 400°C for 15 minutes in vacuum. As-deposited and annealed CZTS films were characterized using range of characterization techniques to study the structural, optical, morphological, and compositional and optoelectronic properties. Annealed sample revealed (112), (220) and (312) planes corresponds to tetragonal kesterite CZTS structure and secondary peaks of CuZn alloy. The optical study shows that the band gap of the as-deposited CZTS film was found to be 1.68 eV. Upon annealing the optical band gap ~ 1.49 eV corresponds to CZTS were estimated from UV-Visible Spectroscopy and photoluminescence. Densely packed, void free and relatively uniform thin films were deposited by electrodeposition technique. The grain size has been increased upon the heat treatment. Copper and zinc rich off-stoichiometric films were deposited at ~1.1 V. Current density-Voltage (J-V) measurements showed Schottkey behavior. The flat band potential and carrier concentration estimated by C-V measurement for annealed CZTS sample was 0.30 V and ~ 2.4 x 10$^{16}$ cm$^{-3}$ respectively.

**Keywords:** CZTS thin films; Kesterite structure; Cyclic voltammetry; Characterization

**Introduction**

It is important to fabricate thin film solar cells with high efficiency from earth abundant, non-toxic and environmentally friendly elements/materials. In this scenario Cu$_2$ZnSnSe/S$_4$ (CZTSe/S) brings new hopes. It is I-II-IV-VI$_4$ promising quaternary kesterite non-toxic semiconductor compound with p-type conductivity [1-5] and large absorption coefficient, 10$^4$ cm$^{-1}$ [2]. Its optical band gap varies from 1.0 eV to 1.5 eV [1-5] by replacing selenium with sulphur. The highest reported efficiency is 12.6% [6]. It can be synthesized by number of techniques such as hydrazine based solution process [7-9], nanoparticles from nontoxic solutions [10], thermal evaporation [11-13], chemical vapor deposition [14], sputtering [15-18], e-beam evaporation [19], electrodeposition using ionic liquids [20-25], spray pyrolysis [26,27] etc. Electrodeposition is one of the easy, scalable, cost-effective and found to be very successful technique. Either single-step or multistep approach has been accepted for the electrodeposition of CZTS absorber layer. Sliupska et al. [28] has grown Sn-Zn-Cu alloy from aqueous bath containing CuSO$_4$, SnSO$_4$ and SnS$_2$ precursors by electrodeposition technique. Tri-sodium citrate was used as complexing agent/supportive electrolyte. Khalil et al. [29] has deposited Cu-Zn-Sn metal alloys on molybdenum substrate from electrolyte containing CuSO$_4$, ZnSO$_4$, Na$_2$S$_2$O$_3$ and K$_2$P$_2$O$_7$. CZT alloy thin films were subsequently annealed in elemental sulphur for the formation of CZTS. Valdes et al. [30] has electrodeposited CZTS thin films by electrochemical atomic layer deposition and conventional one-step electrodeposition. The deposition of non-stoichiometric CZTS films is reported by one-step electrodeposition. Here we report the synthesis of Cu$_2$ZnSnS$_4$ (CZTS) onto FTO substrate by single-step electrodeposition from aqueous bath. The preliminary results obtained from the pristine and annealed thin films are discussed.

**Experimental Details**

The CZTS films have been synthesized on FTO substrate by cathodic potentiostatic electrodeposition technique at pH 4.5 and bath temperature 50°C with moderate stirring. CuCl$_2$, ZnCl$_2$, SnCl$_2$ and Na$_2$S$_2$O$_3$ were used as precursors for the co-deposition of Cu, Zn, Sn and S, respectively. Tri-sodium citrate is used as complexing agent for the stoichiometric co-deposition of precursors [23,28,30-32]. A standard three-electrode system consisting working, counter and reference electrodes was employed for the electrodeposition of CZTS films. Commercially available fluorine doped tin oxide (FTO) coated soda lime glass substrates of resistivity 10-15 $\Omega$sq, platinum sheet and Ag/AgCl were used as working, counter and reference electrode, respectively. Potentiostat/galvanostat Model, Biologic SP 300 was used to perform the cyclic voltammetry (CV) and electrodeposition of CZTS thin films. Prior to the experimentation, all substrates were thoroughly cleaned using double distilled boiled water, acetone and iso-propanol followed by few minutes ultra-sonication with iso-propanol. The CV experiments were performed for various bath temperatures and stirring rate to optimize the suitable deposition potential for co-deposition of Cu, Zn, Sn and S. Deposition potential -1.1 V was optimized by using cyclic voltammetry experiments. The samples were annealed in vacuum at 400°C for 15 minutes. The pristine and annealed samples were studied by range of characterization techniques to study structural, optical, morphological, compositional and electrical properties. X-ray diffractometer (Model Bruker D8 Advance, Germany) of Cu Kα radiation, with $\lambda$=0.154 nm was used to study the structural properties. Optical measurements were performed using JASCO, UV-VIS-NIR Spectrophotometer model V-670. Photoluminescence was studied by

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Perkin Elmer LS-55 Spectrophotometer, JEOL JSM-6360 A SEM/EDAX at accelerating voltage 20 kV and probe current 1 nA was used to study the surface morphology and elemental composition. Current density-Voltage (J-V) measurements were performed using the Potentiostat/ galvanostat Model, Biologic SP 300. Frequency response analyzer (FRA) facility available in above mentioned potentiostat was used to study the C-V measurements at frequency 100 Hz.

Results and Discussion

Cyclic voltammetry

The cyclic voltammogram recorded with respect to Ag/AgCl reference electrode in the bath consisting precursors of Cu, Zn, Sn and S is shown in Figure 1. The temperature of the bath was maintained at 50°C with continuous stirring with 180 rpm throughout the experimentation. The redox potentials of Cu, Zn, Sn and S are different; therefore the co-deposition of these elements is difficult. However with the help of complexing agent the stoichiometric deposition can be obtained. The complexing agent can slow down the rate of reaction by forming complex or ligands with the noble ionic species. The cathodic and anodic curves are marked by forward (black) and reverse (red) arrows. During the cathodic scan, up to ~0.6 V, current was nearly steady indicates the applied growth potential was not sufficient to deposit the precursors. The current found to be increased beyond ~0.6 V to -0.9 V could be due to the metallic deposition of copper and zinc. The small plateau region revealed around ~1.0 V to -1.1 V ('A') could be due to the metallic deposition of copper and zinc. The sharp linear rise in current at accelerating voltage 20 kV and probe current 1 nA was used to study the formation of enthalpy for CZTS from their respective elements. An important issue regarding the phase formation with quaternary semiconductors is whether homogeneous samples can be synthesized experimentally, or some secondary phases are also unintentionally formed. People must satisfy the following equation:

\[ \Delta H_f = \mu_{Cu} + \mu_{Zn} + \mu_{Sn} + 4 \mu_S = -4.21 \text{ eV} \]  

where \( \Delta H_f \) represents the formation of enthalpy for CZTS as compared to the secondary phases Walsh et al. [34] has calculated the chemical stability region in the atomic chemical potential. To maintain chemical stability region in the atomic chemical potential. To maintain the formation of enthalpy of the particular phase. An important issue regarding the phase formation with quaternary semiconductors is whether homogeneous samples can be synthesized experimentally, or some secondary phases are also unintentionally formed. People have grown CZTS samples successfully using a variety of techniques (vacuum and non-vacuum; solution and solid-state) reported above, and significant variation has been achieved in the Cu: Zn: Sn atomic ratio, depending on the growth environment. If secondary phases are formed during the synthesis, these phases can be removed upon annealing in inert atmosphere. To describe the phase stability of CZTS as compared to the secondary phases Walsh et al. [34] has calculated the chemical stability region in the atomic chemical potential. To maintain a stable CuZnSnS4 crystal, the chemical potentials of Cu, Zn, Sn and S must satisfy the following equation:

\[ 2 \mu_{Cu} + \mu_{Zn} + \mu_{Sn} + 4 \mu_S = -4.21 \text{ eV} \]  

where \( \Delta H_f \) represents the formation of enthalpy for CZTS from their respective elements. Both factors i.e., variation of Cu:Zn:Sn:S ratios and annealing treatment controls the chemical potential which shows the stable phase of CZTS within a narrow thermodynamic window.

Secondary phases observed at 42.8° and 49.8° corresponds to CuZn metallic alloy. It is also noticed that depending upon the enthalpy of the complexed ionic species towards the electrode was maintained with continuous stirring. The number of samples were scanned during cyclic voltammetry experiment to optimize the deposition potential and it was found to be ~ -1.1 V with respect to Ag/AgCl reference electrode. The reduction of copper, zinc, tin and sulphur occurs by the following reaction mechanism [33]:

\[ Cu^{2+} + 2e^- \rightarrow Cu(S) \]  \hspace{1cm} (1)
\[ Zn^{2+} + 2e^- \rightarrow Zn(S) \]  \hspace{1cm} (2)
\[ Sn^{2+} + 2e^- \rightarrow Sn(S) \]  \hspace{1cm} (3)
\[ Na_{2}S_{2}O_{3} \rightarrow Na^{2+} + S_{2}O_{3}^{2-} \]  \hspace{1cm} (4)

The deposition of sulphur is not straight forward. In the present bath SnCl2 and Na2S2O3 are used as sources of Sn and S respectively. Both the sources are strong reducing agents which can reduce the copper and zinc; therefore copper and zinc rich layers can be deposited. Upon the application of deposition potential Na2S2O3 may decomposes by the following reaction mechanism.

\[ \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}^{2+} + \text{S}_2\text{O}_3^{2-} \]  

The deposition of the complexes and ligands on the CuZn surface. The reported reduction potential for Cu, Zn and Sn [33] with respect to normal hydrogen are +0.34 V, -0.763V and -0.136 respectively.

X-ray diffraction

The XRD pattern of (a) as-deposited and (b) annealed CZTS sample is shown in Figure 2. FTO peaks are marked by dark solid circles (•). In as-deposited sample, the two peaks present at 43.26° and 50.15° corresponds to (210) and (020) planes of CuZnSnS4 respectively [JCPDF file No. 14-1435]. The broad hump ranging from 20-28° corresponds the mixed amorphous and crystalline nature having short range periodicity of mixed ternary and quaternary phases of CuZnSnS4 or CZTS materials.

Upon heat treatment the broad hump is disappeared and the peaks exhibited at 28.56°, 47.61° and 56.71° corresponds to (112), (220) and (312) planes of CZTS of tetragonal kesterite structure [JCPDF file 26-0575]. The transfer of one phase to another phase depends on the formation of enthalpy of the particular phase. An important issue regarding the phase formation with quaternary semiconductors is whether homogeneous samples can be synthesized experimentally, or some secondary phases are also unintentionally formed. People have grown CZTS samples successfully using a variety of techniques (vacuum and non-vacuum; solution and solid-state) reported above, and significant variation has been achieved in the Cu: Zn: Sn atomic ratio, depending on the growth environment. If secondary phases are formed during the synthesis, these phases can be removed upon annealing in inert atmosphere. To describe the phase stability of CZTS as compared to the secondary phases Walsh et al. [34] has calculated the chemical stability region in the atomic chemical potential. To maintain a stable CuZnSnS4 crystal, the chemical potentials of Cu, Zn, Sn and S must satisfy the following equation:

\[ 2 \mu_{Cu} + \mu_{Zn} + \mu_{Sn} + 4 \mu_S = -4.21 \text{ eV} \]  

where \( \Delta H_f \) represents the formation of enthalpy for CZTS from their respective elements. Both factors i.e., variation of Cu:Zn:Sn:S ratios and annealing treatment controls the chemical potential which shows the stable phase of CZTS within a narrow thermodynamic window.

Secondary phases observed at 42.75° and 49.83° corresponds to CuZn metallic alloy. It is also noticed that depending upon the enthalpy...
or free energy formation of Cu-Zn phase observed in as-deposited sample has been disappeared upon annealing and transformed into Cu-Zn alloy due to the desired condition of free formation of Cu-Zn phase.

**UV-Visible spectroscopy**

The optical study of as-deposited and annealed CZTS sample deposited at -1.1 V is carried out by UV-Visible –IR spectroscopy. Figure 3 depicts the \((\alpha h\nu)^2\) verses energy \(h\nu\) of (a) as-deposited and (b) annealed CZTS thin films. The optical band gap of as-deposited CZTS sample is found to be 1.68 eV. The large band gap value of as-deposited sample could be due to the short range crystallinity, presence of mixed secondary and ternary phases along with metallic phases which agrees well with XRD results. The reported band gap for Cu2ZnSnS4 is ~1.5 eV [1-5], however, due to variation in the chemical composition of the precursors and/or mixed surface morphology and grains size may affect on the band gap of CZTS, which can be varied in the range 1.4 eV to 1.6 eV [35,36]. Upon annealing the band gap estimated ~ 1.49 eV corresponds to CZTS. It is also noticed that after annealing the sample, the absorption intensity was found to be increased by one order of magnitude as compared to as-deposited sample.

**Photoluminescence**

Photoluminescence of (a) as-deposited and (b) annealed CZTS samples were studied by Perkin Elmer LS-55 Spectrophotometer and shown in Figure 4. The small shoulders observed in both as-deposited and annealed samples at 826 nm and 836 nm, respectively are associated with CZTS [1-5]. The peak exhibited around 702 nm could be associated with the ternary and quaternary alloys of CZTS. The highest intensity peak exhibited about 656 nm (1.89 eV) is associated to the formation of ternary alloys of CuZnS [37,38].

**Scanning electron microscopy (SEM)**

The morphology of CZTS samples were studied by scanning electron microscopy (SEM). Figures 5a and 5b depicts the SEM images of as-prepared and annealed CZTS thin films respectively. The compact and well adherent CZTS layers were deposited by electrodeposition technique at -1.1 V. It can be clearly seen from Figure 5 that the small grains are agglomerated in both as-prepared and annealed sample to form the clusters. The enhancement in the size of cluster upon annealing could be clearly seen. As both SEM images were obtained for same magnification, therefore the scale bar given in each SEM image can be used to estimate the cluster size. The particle size was found to be spherical because of the higher concentration of metallic copper and zinc. The grain size in the as-deposited film was ~1 µm whereas after annealing it is found to be increased ~3–4 µm. A cauliflower like morphology has been observed in both as-deposited and annealed samples.

**Energy dispersive spectroscopy (EDS)**

The elemental composition of (a) as-deposited and (b) annealed CZTS films was studied by energy dispersive spectroscopy and summarized in Table 1. The elemental composition of as-deposited film is, Cu=48.28, Zn=27.89, Sn=8.82 and S=20.41, whereas after annealing it is Cu=48.03, Zn=27.89, Sn=8.82 and S=15.26. CZTS films are found to be copper and Zn rich. The sample close to the stoichiometry could be deposited by optimizing the concentration of complexing agent and/or pH and temperature of the bath (Figure 6).
Current density – Voltage (J-V) measurement

The current density–voltage (J-V) measurement of as-deposited and annealed sample studied under dark condition is depicted in Figure 7. Both as-prepared and annealed CZTS sample shows Schottky behaviour under dark condition. The potential barrier, \( \phi_b \), was calculated by the following equation [39];

\[
\phi_b = \frac{kT}{q} \ln \left( \frac{A^*T^2}{J_s} \right)
\]

(6)

where, \( \phi_b \) is the barrier height, \( k \) is the Boltzmann's constant, \( T \) is the temperature, \( q \) is the charge on electron, \( A^* \) is the effective Richardson's constant for CZTS (63.6 A/cm² K²) [40] and \( J_s \) is the reverse saturation current density. The barrier height \( \phi_b \) was found to ~ 0.29 eV and 0.26 eV for as-deposited and annealed CZTS sample, respectively. The barrier height \( \phi_b \) is found to be decreased upon annealing the sample. This is associated with several parameters viz. the crystallinity of the layer, the formation of homogeneous mixture of ternary/quaternary alloy, presence of secondary phases, grain boundaries and nature of metal semiconductor contact.

Capacitance – Voltage (C-V) measurement

The capacitance – voltage measurement of (a) as-deposited and (b) annealed CZTS sample was performed under dark condition with frequency 100 kHz and plots are shown in Figure 8. The observed Mott-Schottky plots of both as-deposited and annealed samples were nearly similar except small change in the flat band potential. The inversion, depletion and accumulation region are observed in both as-deposited and annealed samples however, inversion region is very small. The inversion and depletion region are related to the depletion of the charge carriers whereas accumulation is related to diffusion of the charge carriers. The values of flat band potential are found to be 0.36 V and 0.30 V for as-deposited and annealed CZTS sample respectively. The carrier concentration is calculated by using the following relation [39,40].

\[
N_d = \frac{2}{e\varepsilon_k} \left[ \frac{1}{d(V/C^2)/dV} \right]
\]

(7)

Elemental Composition in At. %

<table>
<thead>
<tr>
<th>Deposition potential (V)</th>
<th>Sample condition</th>
<th>Cu</th>
<th>Zn</th>
<th>Sn</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.1 V</td>
<td>As-deposited</td>
<td>48.28</td>
<td>21.88</td>
<td>9.43</td>
<td>20.41</td>
</tr>
<tr>
<td></td>
<td>Annealed</td>
<td>48.03</td>
<td>27.89</td>
<td>8.82</td>
<td>15.26</td>
</tr>
</tbody>
</table>

Table 1: A summary of elemental compositions obtained by EDAX for as-deposited and annealed Cu₂ZnSnS₄ sample.

Figure 5: SEM micrographs of CZTS thin films, (a) as-deposited and (b) annealed at 400°C for 15 minutes.

Figure 6: EDS spectra of CZTS thin films, (a) as-deposited and (b) annealed at 400°C for 15 minutes.

Figure 7: J-V characteristics of (a) as-deposited and annealed CZTS thin films at 400°C for 15 minutes.
The value of static relative dielectric constant of CZTS material is taken 4.27 [10] for calculation of carrier concentration. The carrier concentration of the as-deposited film was found to be 1.4 × 10^{18} cm^{-3}. Upon annealing the carrier concentration was calculated − 2.4 × 10^{16} cm^{-3} which is very similar to that of as-deposited sample. Further optimization in annealing condition is under progress to obtain the photoactive semiconductor layers.

Conclusions

In conclusion, CZTS thin films can be deposited by low-cost electrodeposition technique. XRD results revealed (112), (220) and (312) planes corresponds to tetragonal kesterite CZTS structure. The optical band gap of the as-deposited CZTS film was found to be 1.68 eV. Upon annealing the band gap was estimated − 1.49 eV corresponds to CZTS which was further confirmed by photoluminescence study. Cauliflower like morphology of grain size 3 - 4 μm was observed upon annealing the CZTS sample. EDS data confirms the deposition of off stoichiometric CZTS films. The elemental composition of as-deposited film was Cu=48.28, Zn=21.88, Sn=9.43 and S=20.41, whereas, upon annealed the composition were Cu=48.03, Zn=27.89, Sn=8.82 and S=15.26. Both as-prepared and annealed CZTS sample showed Schottky behaviour under dark condition. The carrier concentration calculated from Mott-Schottky plot was found to be in the order of −10^{16} cm^{-3}. The deposition of highly crystalline CZTS layers with desired composition close to the ideal is under progress.

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References