Effect of Copper Content on Structural, Morphological, Optical and Photoelectrochemical Properties of SILAR Deposited Cu$_3$SnS$_4$ Thin Films

Harshad D. Shelke, Abhishek C. Lokhande, Jin H. Kim and Chandrakant D. Lokhande

Abstract

In this study, Cu$_3$SnS$_4$ (CTS) thin films were deposited by successive ionic layer adsorption and reaction (SILAR) method at room temperature. X-ray diffraction, Raman spectroscopy, scanning electronic microscopy, Ultra-violet-visible-near infrared absorbance spectroscopy and photoelectrochemical analyses were used to follow the evolution of the investigated properties. The results outlined a tetragonal (1-42m) CTS phase and a secondary copper sulfide (Cu$_2$S) and Cu$_3$SnS$_4$ phase, and their ratio strongly depends on the copper concentration. No traces of secondary phases of tin sulfide is found while CTS was obtained. It was found that the application of additional Cu concentration increases from 0.025 to 0.075M, enhances the grain growth in size and induces significant improvement of CTS crystallinity and power conversion efficiency. The optical band gap ranges between 1.90, 1.21 and 1.07eV depending on the copper concentration 0.025, 0.050 and 0.075 M, respectively. This study shows promising results, as a developing photovoltaic applications, using SILAR CTS as absorber.

Keywords: Band gap; Cu$_3$SnS$_4$; Optical properties; Molarity; Nanocrystals.

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1. Introduction

Last few decades, the copper based multinary compound semiconductor materials are used as absorber materials in photovoltaic technology. Cu$_2$ZnSnS$_4$ (CZTS) has been regarded as the alternative absorber layer to Cu(In,Ga)Se$_2$ due to its earth abundance and eco-friendly ingredients, optimal direct band gap of 1.45 eV and high absorption coefficient in the visible range. But compositional control and growth of single phase CZTS films are quite difficult to be processed. The control of composition and phase structure in Cu$_3$SnS$_4$ compound is more convenient due to its fewer elements compared with CZTS.

In particular, copper-based Cu$_3$SnS$_4$, including Cu$_2$SnS$_3$, Cu$_3$SnS$_4$, Cu$_3$SnS$_4$, Cu$_3$SnS$_7$, Cu$_3$SnS$_7$, etc., is an ideal candidate material for solar cell and photocatalysis applications owing to its high photocatalytic activities towards hydrogen evolution, high absorption coefficient (>10$^4$ cm$^{-1}$) in the visible spectral range and proper band gap order (0.93 to 1.35 eV). Currently, Cu$_3$SnS$_4$ (CTS) based ternary semiconductors have grown more interests as significant ternary I-IV-VI group semiconductors with diminutive or mid band gap. Eco-friendly, low cost and non-toxic nature of CTS similar to that of CZTS material has fascinated immense attention due to its wide-ranging applications in photovoltaic devices. The renewable energy resources necessitate to use new materials in optoelectronic applications. In recent period, CTS has received rising consideration as a promising photovoltaic material for scalable production of thin film solar cells because of its non-toxic and earth abundant elements, and a tunable direct band gap of 0.9 to 1.5eV. As for the synthesis methods of CTS compound, a few studies have been reported on chemical methods such as chemical bath deposition (CBD), [8] electrodeposition, [9] successive ionic layer adsorption and reaction (SILAR), [10] ball milling, [11] solvothermal, [12] etc.

Among these chemical methods, SILAR is a simple, less expensive and less time consuming method for the deposition of semiconductor thin films. In SILAR method, sufficient reaction time favors the complete chemical reaction and hence produces pure phase compounds without secondary phases. In the present work, CTS thin films have been synthesized by the SILAR method. There are only a few reports existing for the deposition of CTS thin films using the SILAR method. The
aim of this present work is showing the effects of the material composition (such as copper content) on the structural, morphological, optical and electrical properties of CTS thin films.

2. Experimental

2.1 Synthesis of CTS material

CTS thin films were deposited on ultrasonically cleaned soda lime glass (SLG) and fluorine doped tin oxide (FTO) substrates by the SILAR method. The chemical approach was applied to synthesize CTS thin films. The mixed solution of copper chloride (CuCl₂:2H₂O), tin chloride (SnCl₂:2H₂O) and triethanolamine (TEA) was used as the cationic precursor and sodium sulfide (Na₂S.xH₂O) solution was used as an anionic precursor. In the deposition process of CTS, triethanolamine solution was used as a complexing agent to bind metal cations in the solution. The CTS precursor solution contained copper chloride (0.025-0.075 M), tin chloride (0.025 M) and sodium sulfide (0.1 M).

In the SILAR method, the substrate was immersed into separate cationic and anionic precursor solutions for the adsorption and reaction, and then rinsed with double-distilled water (DDW) after each immersion to remove the loosely bound particles and to avoid the precipitation. By repeating the cycle described above, the CTS thin film with the desired thickness was obtained by adjusting the preparative parameters. These films were annealed for 3 hours at 300 °C in a vacuum to improve the crystallinity. The CTS films were well adherent, uniform and blackish in color.

To study the effect of copper salt concentration on the formation of CTS films, copper chloride in the solution varied from 0.025 - 0.075 M in the steps of 0.025 M. These samples were further used for structural, morphological, optical and photoelectrochemical (PEC) properties. The samples were denoted as ‘S1’ for copper 0.025 M, ‘S2’ for copper 0.050 M and ‘S3’ for copper 0.075 M, respectively.

2.2 Materials characterization

After film layers had been developed, the structural, morphological, optical and electrical properties were characterized. The structural characterization of CTS nanoparticles was carried out using X-ray diffraction (XRD) by BRUKER AXS D8 Advanced model X-ray diffractometer equipped with Cu radiation (Kₐ of λ= 1.54 Å) operated at 40 kV. Raman spectra were recorded in the range of 150–500 cm⁻¹ by using a micro-Raman spectrometer (Via Reflex UV Raman microscope, Renishaw, U.K. at KBSI Gwangju center) using a He–Ne laser source. The morphological features of CTS nanoparticles were analyzed by scanning electron microscopy (SEM) JEOL JSM-6390. SEM technique was used to observe the grain size, rough morphology, and distribution of the particles on the surface of the system. The UV–visible optical absorption and transmittance spectra of CTS thin films had been carried out to explore their optical properties. The optical analysis was carried out by a HITACHIV UV4100 spectrometer in the wavelength ranging from 310 to 900 nm at room temperature. The current density-voltage (J-V) characteristics of the PEC cell were observed using a Princeton Applied Research Potentiostat (273A) with a CTS electrode as the working electrode.

Fig. 1 XRD patterns of a) CTS thin films prepared at different copper concentration: S1 = 0.025 M, S2 = 0.050M and S3 = 0.075M; b) XRD spectra of diffraction angles, 2θ, around 28° at copper concentration: S1 = 0.025M, S2 = 0.050M and S3 = 0.075M and c) diffraction angles, 2θ, around 47° at copper concentration: S1 = 0.025M, S2 = 0.050M and S3 = 0.075M.
3. Results and discussion

3.1 Structural studies

Fig. 1a confirms the XRD patterns of CTS films deposited with different molar concentrations such as 0.025, 0.050 and 0.075 M as denoted by S1, S2 and S3, respectively. The XRD pattern gives an idea that the deposited films possess tetragonal (I-42m) structure with a polycrystalline nature (JCPDS No. 00-033-0501) of Cu3SnS4 material. For the sample S1 prepared with 0.025 M concentration, a small peak located at the angle 28.69° emerges in the XRD patterns. At 0.050 M concentration, the strong peaks at 47.11° are assigned to (0-010) plane regarding the triclinic phase (JCPDS 00-027-0198) of Cu2SnS3 material in S2 sample. Further increase the molar concentration to 0.075 M, the formation of a higher Cu content compound (Cu4SnS4) was observed with a tetragonal (I-42m) structure. This result is expectable due to the reaction mechanism between Cu and S.

The strongly oriented peaks at 2θ = 28.9°, 47.62° and 57.01° corresponded to the diffraction planes along the (112), (220) and (132) direction respectively. As the intensity of these planes is observed higher in sample S3 compared to others. Furthermore, the diffraction pattern could also match other CTS secondary phase such as Cu2SnS3 (JCPDS Card: 00-027-0196). This is because of an excess of CuCl2 in the solution. The main information that could be deduced from the XRD patterns is the presence of copper sulfide (Cu2S,S) in a covellite structure (JCPDS Card: 00-079-2321) and, especially the absence of secondary materials such as other binary compounds (CuS, SnS2 and SnS). Further, it is seen that as the Cu concentration increases from 0.025 to 0.075 M, the intensity of prominent peak increases. The intensity of the peaks was moderately augmented as the Cu concentration was enhanced along with secondary phases. Similar effects were also observed by Kermadi et al. during the CZTS formation.[13] Hence, it is concluded that the secondary phase assists the formation of CTS film through liquid assisted grain escalation, resulting in large grains and compact nature of CTS films.

Fig. 1 shows the detailed spectra of the three samples at diffraction angles, 2θ, around 28° and 47° denoted as (b) and (c), respectively. The phase assignment and crystallites orientation were performed using the JCPDS database. Despite the fact that triclinic Cu2SnS3 and tetragonal phases of Cu3SnS4 present the peaks close to each other, the detailed analysis shown allow a clear assignment. In the detailed XRD patterns of Cu3SnS4 compound at the 2θ close of 28.9°, a deviation from the JCPDS database value is observed. This fact may be related to the presence of strain in the sample.[14]

3.2. Raman Analysis

To confirm the crystal structure and phase formation of the films, Raman spectra of CTS samples were studied. Raman spectroscopy gives the characteristic vibrational modes of bulk CTS, other secondary and co-existing phases, which can be differentiated from each other. The Raman spectra of CTS films deposited with different molar concentrations are shown in Fig 2. In the Raman spectra, the observed peaks at 252, 291, 318, 322 and 471 cm−1 are related to various optical phonons modes of CTS phase. As seen in Fig 2, for the samples S1 and S2 prepared with 0.025 and 0.050 M concentration, the observed low-intensity modes at 291 and 320 cm−1 are close to the reported Raman modes of triclinic CTS.[15] The modes at 291 and 318 cm−1 are endorsed to tetragonal CTS phase, which is in concurrence with the result reported for Raman analysis at S3 sample.[9] According to the XRD analysis, these peaks are attributed to Tetragonal (I-42m) Cu3SnS4.

In addition, the presence of shoulder peak at 291 and 322 cm−1 confirms the formation of tetragonal Cu3SnS4, which is because of an excess of CuCl2 in the cationic solution.[16] These results also show the presence of Cu2S with the characteristic Raman peak at 251 and 470 cm−1.[17] With Cu-rich conditions, the neighboring compound of Cu2SnS3 is Cu3SnS4 in the Gibbs phase triangle.[18] Cu2SnS3 is relatively stable and can be grown at room temperature.[19] In fact, the calculated chemical potential phase space of Cu-Sn-S system showed that Cu3SnS4 has a wide thermodynamic window of stability.[20] Thus, the formation of that ternary could also occur in spite of Cu-rich content compound. The formation of mixed phase of Cu3SnS4 along with secondary phases of Cu2SnS3 and Cu2-xS is due to the Cu-rich composition prepared using the single step SILAR method. Thus, it is clear that due to different molar concentrations of copper in the single cationic bath, it is very difficult to deposit CTS thin films with phase purity and stoichiometric composition.

![Fig. 2 Raman spectra of CTS thin films prepared at copper concentration: S1 = 0.025 M, S2 = 0.050 M and S3 = 0.075 M.](image-url)

3.3 SEM Analysis

Fig. 3 shows SEM micrographs of CTS films deposited from solutions having different copper salt concentrations. The results show that all the surfaces are homogeneous and mainly composed of spherical grains with some large sparse clusters and spherical shape. The micrograph of films deposited from a solution with 0.025 M copper salt concentration, Fig. 3 (S1), shows a smeary appearance with large island-like regions. As the copper salt concentration in the solution is increased up to 0.050 M, distinct grains are seen in the film formed (see Fig. 3 (S2)). When the copper concentration in the solution is further increased to 0.075 M, agglomeration of the grains is...
found to occur, Fig. 3 (S3). In sprayed CZTS, Kumar et al.
observed similar types of grains increasing in size with increasing the Cu content. An increase in the surface clusters with increasing the Cu salt concentration indicates a possible further reaction of the films on the most active sites, confirming the aforementioned reports. This effect reaches its maximum for the 0.075 M sample and proves that the reaction completion can be different according to the copper content. The increase of Cu content implies an increase in the mean grain size from 100 up to 300 nm. It is also useful to mention that the Cu-poor sample leads to cluster-like aggregates, while by increasing the copper amount, the aggregates are rounded and more size-random. This increase in the grain size might be due to the agglomeration of grains. Increase in grain size improves the performance of a polycrystalline CTS thin film with a decrease in grain boundaries that increases the effective diffusion length of minority carriers.

3.4 Optical analysis

To evaluate the optical band gap for different samples, the relation between the direct energy gap ($E_g$) and absorption coefficient ($\alpha$) from the Tauc's approximation was shown in Equation 1:

$$\alpha(\lambda) = \frac{A(h\nu - E_g)^n}{h\nu}$$

(1)

where $A$ is a proportionality constant, $h$ is the Planck's constant and $n$ defines the nature of the radiative transition. In the present investigation, the values of $n$ are found to obey the above Equation for $n=1/2$, indicating that the optical transitions are direct-allowed in nature. The effect of Cu concentration on the optical characteristics such as coefficient of absorption and band gap of CTS thin film was investigated. Fig. 4(A) demonstrates the absorption spectra of CTS film with different Cu concentration. The energy band gap of CTS thin films was determined from the optical absorption study in the wavelength having the range of 300–900 nm, which is important in the design and analysis of various optical devices. Fig. 4 (B) shows a plot of the square of the product of the absorption coefficient and photon energy as a function of the photon energy for the SILAR deposited CTS films with different Cu concentrations.

The band gap is estimated by extrapolating the straight line part of the $(\alpha h\nu)^2$ versus $h\nu$ curve to the intercept of the horizontal axis. The values of band-gap for CTS films are determined to be 1.90, 1.21 and 1.07 eV for 0.025, 0.050 and 0.075 M, respectively. The decrease in the band gap with an increase in the Cu concentration may be because of: 1) increase in the crystallinity observed from XRD analysis, 2) excess of Cu ionsin the cationic bath solution and 3) The presence of secondary phase Cu$_2$SnS$_4$ carrying a narrow band gap observed from XRD and Raman analysis. The band gap tunneling may be understood according to the symmetry of the valence band maximum (VBM) and conduction band minimum (CBM) states.

3.5 Photoelectrochemical cell (PEC) analysis

The PEC performance of the CTS thin films deposited on the FTO substrates with different Cu concentrations was investigated using the linear sweep voltammetry (LSV) measurements. The LSV was performed in a lithium perchlorate (0.5 M LiClO$_4$) electrolyte under AM 1.5G (100 mWcm$^{-2}$) illumination using a conventional two electrode system with a CTS photocathode and graphite as a working electrode and counter electrode, respectively. The illuminated $J$-$V$ curves for CTS based PEC devices fabricated using 0.025, 0.050 and 0.075 M are shown in Fig. 5. The PEC characterization is selected because it is easier than forming a solid-state junction. It allows a rapid and nondestructive
evaluation of a photoactivity of the CTS thin films. The photovoltaic output characteristics of CTS thin films are analyzed by fabricating FTO/CTS/0.5 M LiClO$_4$/C cell. The anodic photocurrent was enhanced with the negative potential, which designates the p-type conductivity of deposited CTS thin films.$^{[28]}$

Fig. 4 (A) Optical absorption and (B) Variation of $(\alpha h \nu)^2$ versus $(h \nu)$ plot of CTS thin films prepared at a copper concentration: S1 = 0.025 M, S2 = 0.050 M and S3 = 0.075 M.

Fig. 5 $J$-$V$ characteristics of CZTS thin films prepared at copper concentration: S1 = 0.025 M, S2 = 0.050 M and S3 = 0.075 M.

Table 1. Solar cell parameters of PEC devices fabricated for different copper concentration: S1 =0.025 M, S2 = 0.050 M and S3 = 0.075 M.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Sample</th>
<th>$J_{sc}$ (μA)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{max}$ (μA)</th>
<th>$V_{max}$ (mV)</th>
<th>Fill Factor (FF) (%)</th>
<th>Efficiency η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>S1</td>
<td>79.70</td>
<td>48.00</td>
<td>33.78</td>
<td>28.78</td>
<td>0.254</td>
<td>0.001</td>
</tr>
<tr>
<td>2.</td>
<td>S2</td>
<td>397.3</td>
<td>405.0</td>
<td>223.7</td>
<td>178.3</td>
<td>0.248</td>
<td>0.069</td>
</tr>
<tr>
<td>3.</td>
<td>S3</td>
<td>469.6</td>
<td>521.6</td>
<td>267.9</td>
<td>214.7</td>
<td>0.239</td>
<td>0.114</td>
</tr>
</tbody>
</table>

In the dark, the PEC cell device exhibits diode like characteristics, which shows an insignificant reverse saturation current. While the $J$-$V$ characteristics under illumination appear the images of a linear plot. These linear manners of $J$-$V$ plots are mostly ascribed to the digression from the stoichiometry, extensively elevated series resistance of absorber layer and the squat shunt resistance of the PEC device. The detailed PEC parameters are listed in Table 1. The significant enhancement in the $J_{sc}$ and $V_{oc}$ is observed with increasing the Cu concentration upon illumination as shown in Fig. 5. It can be clearly seen from the graph that the solar cell based on CTS thin films derived from 0.025 M concentration denoted by S1 shows a relatively poor performance. This may be due to an insufficient Cu concentration during the CTS formation process, which may create structural defects in the CTS film. While the cell derived from 0.075 M concentration denoted by S3 exhibits a better conversion efficiency of 0.11 %. From the structural analysis, it is observed that the S3 sample shows a very small secondary phase of Cu$_2$S and Cu$_4$SnS$_4$. The 0.025 and 0.050 M concentration films show a low efficiency as compared to 0.075 M films.

The fill factor (FF) is lower in the present PEC devices because of impurities and defects, including insulating secondary phases, which cause charge carrier recombination. This effect would be a similar to that of sprayed CZTS thin films.$^{[25]}$ The short circuit current ($J_{sc}$) increases with increasing the Cu concentration. This is due to the improved and large grain size, which increases the absorption of incident photons. Additionally, it helps to increase the current generation and reduce the minority recombination rates. Similar results are also mentioned by He et al.$^{[26]}$ The augmentation of these solar cell parameters could be attributed to the improved morphology of CTS thin films, which affected the CTS-electrolyte junction quality and dynamics of charge carrier recombination. Similar effect was introduced by Suryawanshi et al. during the formation of CZTS thin films.$^{[27]}$ The photoelectrochemical measurement confirmed the best photo-activity of the CTS thin films as illustrated in Table 1. The presence of the secondary phases could affect the photovoltaic performance. It has been speculated that the phase separation of CTS into Cu$_2$S and Cu$_4$SnS$_4$ compounds is one of the factors limiting the efficiency of CTS solar cells. In thin-film solar cells, Cu-rich compounds tend to show poor power conversion efficiencies due to their higher electrical conductivity, leading to the shunting problem.$^{[28]}$

4. Conclusions
In this paper, the effects of copper concentration on structural, morphological, optical and PEC properties of CTS thin films have been investigated. The analysis of XRD patterns indicates that the CTS film with a copper concentration up to 0.075 M have a sharp and intense peak orientation. Further, Raman studies confirm the formation of mixed phase of Cu$_4$SnS$_4$ along with secondary phases of Cu$_2$SnS$_2$ and Cu$_5$X$_2$S due to Cu-rich composition. SEM results indicate that as the Cu concentration increases, the average grain size also increases. Decrease in band gap due to increase in copper concentration was confirmed. Furthermore, the solar cell fabricated with the copper rich CTS film (S3) showed an enhancement in the conversion efficiency about 0.11%. Because of the increased number of elements in CTS, their
synthesis is more difficult than for binary and ternary semiconductors. The secondary phases in CTS such as Cu₂SnS₃ and Cu₄SnS₄ could be formed depending on the processing conditions. Experimentally, it is found that working devices are obtained for “Cu-poor” compositions.

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There are no conflicts to declare.

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Author information
Harshad D. Shelke is currently a Ph.D student in Prof. C.D. Lokhande’s group in Thin Film Physics Laboratory (TFPL) at Shivaji University Kolhapur. He received his M.Sc. degree from same University in 2014. He has published 8 papers on Copper based chalcogenide materials with citation over 20 times. His research focused on the Simple chemical processed Cu₂SnS₃ thin film solar cell and its optoelectronic characteristics.

Abhishek C. Lokhande is a Postdoctoral Fellow of Department of Physics, Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates (UAE). He obtained his Ph.D from Optoelectronic Convergence Research Centre, Department of Materials Science and Engineering, Chonnam National University, Gwangju, South Korea under the supervision of Prof. Jin H. Kim. He has...
published over 117 papers on Copper based chalcogenide materials with citation over 2000 times. His current research focuses on thin film photovoltaics using earth-abundant and nontoxic materials.

**Jin H. Kim** is Professor of Optoelectronic Convergence Research Centre, Department of Materials Science and Engineering, Chonnam National University, Gwangju, South Korea. His current research focuses on thin film photovoltaics, Gas-sensor, Photocatalysis, Li-ion batteries and Supercapacitor using earth-abundant and nontoxic materials.

**Chandrakant D. Lokhande** is a Research Director of Center for Interdisciplinary Research Centre, D. Y. Patil University, Kolhapur. He obtained his Master degree and Ph.D degree from Shivaji University Kolhapur. He then did his postdoctoral research at Dept. of Materials Science, Weizmann Institute of Science, Rehovot, Israel worked on CuIn chalcogenide thin films. He was honored “Alexander Von-Humboldt Fellowship, Germany” in 1996-2001 and Nomination for Shanti Swarap Bhatnager Award by Shivaji University, Kolhapur in 1998 & 1999. He has Patents: (46) (Indian 11 accepted, Korean 5 accepted), Applied (Indian) 29, (Korean) 1, World 01. He has published over 600 papers on various materials with cited over 50,000 times. His current research focuses on thin film photovoltaics, Gas-sensor and Supercapacitor using earth-abundant and nontoxic materials.

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