Deposition Time Effect On The Physical Properties Of Cu2ZnSnS4 (CZTS) Thin Films Obtained By Electrodeposition Route Onto Mo-coated Glass Substrates

Taoufik Slimani Tlemçani,a El Bachir Benamar,a Fouzia Cherkaoui El Moursli,a Faiza Hajji,a Zineb Edfout,a Mhamed Taibi,b Hicham Labrim,c Bouchra Belhorma,c Safae Aazoud,d Guy Schmerber,e Karima Bouras,f Zouheir Sekkat,d Aziz Dinia,e Alexander Ulyashin,g Abdelilah Slouif and Mohammed Abd-Lefdi1,a,*

a University of Mohammed V, Faculty of Sciences, P. B. 1014, Rabat, Morocco
b University of Mohammed V, LPCMIN, Ecole Normale Supérieure, Rabat, Morocco
c CNESTEN, Rabat, Morocco
d Optics & Photonics Center, Moroccan foundation for Advanced Science, Innovation and Research (MAScIR), Rabat, Morocco
e IPCMS, UMR 7504, CNRS-Université de Strasbourg, 23 rue du Loess, F-67034 Strasbourg Cedex 2, France
f ICube UMR 7357, 23 rue du Loess - BP 20 CR - 67037 Strasbourg Cedex 2, France
g SINTEF, P. O. Box 124 Blindern, NO-0314 Oslo-Norway

Abstract

Kesterite Cu2ZnSnS4 (CZTS) is a very promising absorber material for low cost and high efficiency thin film photovoltaic cells due to its direct band gap and to its high absorption coefficient. In this work, CZTS layers were deposited onto Mo-coated glass substrates using a single step electrodeposition process. Sulfurization treatment was performed under Argon atmosphere at 500°C. The effect of the deposition time in the range of 10 min- 40 min was investigated. X-ray diffraction and Raman spectroscopy have confirmed the Kesterite structure of all deposited films. The surface morphology of the samples was examined using scanning electron microscopy. Cu/(Zn+Sn) of about 0.80, determined by energy dispersive X-ray spectroscopy, was reached for CZTS films electrodeposited during 30 min. Photoluminescence Spectroscopy showed a broad PL band centered around 1.45 eV.

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* Corresponding author. Tel.: +212 (0) 5 37 77 18 34; fax: +212 (0) 5 37 77 42 61.
E-mail address: a-lefdil@fsr.ac.ma
1. Introduction

Cu2ZnSnS4 (CZTS) has been widely investigated as absorber thin film for solar cells [1]. It can replace Cu(In,Ga)Se2 (CIGS) and CdTe since it consists of non toxic, abundant and cheap elements. It is derived from CuInS2 (CIS) where two In atoms are substituted by one Zn and one Sn atom [2-4]. This isoelectronic substitution results in a material with many of the same properties of the parent compound. Indeed CZTS possesses the desirable properties including p-type conductivity, high absorption coefficient and band gap of around 1.5 eV [5], which makes it leading candidate to further advance thin films photovoltaics.

Recently, there has been huge attraction to work on CZTS based solar cells with a great variety of techniques used to synthesise and study them. Various approaches have been applied to grow CZTS thin films including e-beam evaporation [6], chemical vapour deposition [7], RF sputtering [8], sol gel spin coating [9], pulsed laser deposition [10], chemical bath deposition [11], co-evaporation [12], spray [13,14], ink coating process [15,16] and electrodeposition at room temperature [17-21]. Among all these techniques, electrochemical route is a non-vacuum chemical technique, easy to control and may allow large scale semiconductor deposition and low cost industrial production.

Stoichiometry and crystalline quality of the absorber material play a key role in solar cell performance. Hence, it is very important to understand and optimize the growth and phase formation of the photovoltaic material in order to achieve the desired stoichiometry and the best crystallinity. It is reported that devices using CZTS layers with Zn-rich and Cu-poor compositions show high efficiency, compared to those using stoichiometric CZTS samples [22]. This is due to the fact that the Cu-poor composition enhances the formation of Cu vacancies, which gives rise to shallow acceptors in CZTS, while a Zn-rich condition suppresses the substitution of Cu in Zn sites, which results in relatively deep acceptors [23]. Being quaternary compound, CZTS often contains other binary and ternary phases [24-26] and it is difficult to control the stoichiometry. Thus, it requires very good control over synthesis parameters by changing the deposition parameters such as the precursor’s composition, the bath temperature, the annealing temperature and the deposition time in order to obtain the desired phase of the material.

In the present study, a single step electrochemical growth of CZTS thin films on Mo-coated glass substrates with various deposition times is reported. The structural, compositional, morphological, and optical properties were investigated.

2. Experimental

The CZTS thin films have been prepared by cathodic deposition from an aqueous solution prepared by dissolution of analytical grade reagents of copper sulfate (0.02M), zinc sulfate (0.02M), tin chloride (0.02M), and sodium thiosulfate (0.02M) in distilled water. Citric acid (C6H8O7) was added to reach the desired pH value (between 4-4.5) and sodium citrate (Na3C6H5O7) was used as complexing agent. The solution was magnetically stirred and heated during preparation to get clear and homogeneous solutions.

The electrodeposition cell was a pyrex glass vessel with a three electrode systems consisting of a saturated potassium chloride calomel electrode (SCE), a platinum sheet counter electrode and a Mo/glass working electrode. The electrodeposition was carried out employing a PGZ 301 Voltalab Potentiostat/Galvanostat. CZTS thin films were prepared using single step electrochemical process in potentiostatic mode, applying a potential of -1.1 V with respect to the SCE electrode. In this work, all the samples were deposited at 45 °C bath temperature and without stirring. Mo/glass used as substrate was first cleaned with acetone and rinsed with distilled water and finally dried in air. Completing the electrodeposition, the as-deposited films were rinsed with distilled water and dried in air. The sulfurization process of the films was performed in a tubular furnace using 0.6 g of elemental sulfur (99.99%), under Argon atmosphere during 80 minutes at a temperature of 500°C. Finally, the system was allowed to cool naturally.

The X-ray diffraction (XRD) was performed in a 0-2θ coupled geometry with X’Pert Pro diffractometer with Ni-filtered CuKα radiation (λ=1.5406 Å). Raman spectroscopy was carried out to confirm the phase purity of the films at room temperature using the Horiba’s LabRam ARAMIS spectrometer equipped with a multichannel CCD detection.
system in the backscattering configuration. The incident laser light with the wavelength of 532 nm was used with a power fixed at 9 mW. Surface morphology of the samples was observed by a scanning electron microscope (SEM, JEOL-JSM 6700). The chemical composition of the samples was characterized by an energy dispersive spectrometer (EDS) attached to the JEOL SEM. Photoluminescence (PL) was performed on samples mounted in the closed-cycle He cryostat. The 532 nm laser line was used for PL excitation and the spectra were detected by using a CCD detector.

3. Results and discussion

Fig. 1 shows the XRD patterns of annealed CZTS thin films in sulfur atmosphere at 500°C for different deposition times. The XRD patterns of the CZTS thin films at the deposition time in the range of 10-40 min reveal the distinct diffraction peaks of (112), (200), (220) and (312) planes, which are characteristic of the kesterite structure (JCPDS card no: 00-26-0575 (CZTS)). We also observe peaks attributed to MoS$_2$, most likely as a consequence of sulfurization treatment [27]. The results are in agreement with reports by other groups [17,28]. The degradation of the CZTS film upon deposition at 40 min is also seen in the XRD pattern where the disappearance and the decrease of the peak intensities are observed; (112) and (200) diffraction peaks become relatively smaller and broader. This result agrees with what we have observed during 40 min deposition time because the solution begrimed and became not clear. However, other researchers electrodeposited CZTS films during 40 min but at room temperature [18,20].

![X-ray diffraction patterns of CZTS films electrodeposited at different times.](image)

The XRD coherent crystalline particle size was calculated using Scherrer’s equation:

$$d_{XRD} = \frac{K \cdot \lambda}{\Delta \cdot \cos \theta}$$

Where $\lambda$ is the X-ray incident wavelength, $\Delta$ is the FWHM of the diffraction line; $\theta$ is the angle of diffraction and the constant $K \sim 0.9$. The crystallite size increases with increasing deposition time and was found around 42, 54, 60 nm for $t = 10, 20$ and 30 min, respectively.

CZTS thin films were analyzed by Raman spectroscopy as described in Fig. 2, which was observed in a range of 200-500 cm$^{-1}$. Four main Raman peaks were observed at 255, 286, 330 and 377 cm$^{-1}$ regardless of any deposition time in the range of 10-30 min. No evidence of secondary impurity phases, such as Cu–S and Sn–S, are observed in the Raman spectra [14]. The four main peaks were perfectly matched with the main Raman peaks characteristics of CZTS Kesterite phase [29]. Raman spectroscopy clearly showed a trace of MoS$_2$, which decreased dramatically at
higher deposition time like in the XRD result. The intensity of the $330 \text{ cm}^{-1}$ peak increased with increasing deposition time up to 30 min. Along with XRD results, Raman spectra also indicate that CZTS thin film deposited for 30 min has the better crystallinity.

![Raman scattering spectra of CZTS films electrodeposited at different times.](attachment:image)

**Fig. 2.** Raman scattering spectra of CZTS films electrodeposited at different times.

The SEM surface images of CZTS films deposited at different times are shown in Fig. 3a-c. As depicted, tremendous morphological differences have been observed between the CZTS films. With the increase of deposition time, the surface morphologies of films obviously change. The deposited film at 10 min (Fig. 3a) shows the non-uniform texture, some voids or cavities and cauliflower-like appearance. For a deposition time of 20 min (Fig. 3b), the SEM image shows more apparent grain structures and the surface morphology becomes homogeneous. As the deposition time increased up to 30 min, the film surface becomes more compact with large densely packed grains. So, we conclude that the surface morphology is strongly dependent on the deposition time.

![SEM images of the electrodeposited CZTS films for 10 min (a), 20 min (b) and 30 min (c).](attachment:image)

**Fig. 3.** SEM images of the electrodeposited CZTS films for 10 min (a), 20 min (b) and 30 min (c).

The chemical composition of CZTS thin films has been measured by EDS as shown in Table 1. From the values in the table, nearly stoichiometric compositions are obtained for all deposited CZTS thin films. One can note that the composition ratio of $\text{Cu/(Zn + Sn)}$ in the deposited film decreased as the deposition time increased. CZTS Cu-poor and Zn-rich are appropriate for use as absorber layer in thin film solar cells [30].
Table 1. Chemical composition of CZTS thin films deposited at different time.

<table>
<thead>
<tr>
<th>Deposition time (min)</th>
<th>Cu (at%)</th>
<th>Zn (at%)</th>
<th>Sn (at%)</th>
<th>S (at%)</th>
<th>Cu(Zn + Sn)</th>
<th>Zn/Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>16.61</td>
<td>9.40</td>
<td>9.06</td>
<td>64.93</td>
<td>0.89</td>
<td>1.03</td>
</tr>
<tr>
<td>20</td>
<td>21.39</td>
<td>11.90</td>
<td>13.89</td>
<td>52.82</td>
<td>0.83</td>
<td>0.85</td>
</tr>
<tr>
<td>30</td>
<td>22.12</td>
<td>12.51</td>
<td>15.05</td>
<td>50.32</td>
<td>0.80</td>
<td>0.83</td>
</tr>
</tbody>
</table>

The room temperature photoluminescence (PL) spectra of CZTS thin films are shown in Fig. 4. The observed broad band has a maximum of intensity at 1.45 eV, corresponding to the optical band gap of the CZTS. Thereby, the PL band has an asymmetric shape that is typical for semiconductors with high defect concentration (atomic vacancies, substitutions, interstitials, Cu-Zn antisite …), which is in agreement with previous works [31,32]. This is of particular importance for materials like CZTS. So, the photoluminescence carries useful information that can facilitate sample analysis and augment the Raman data.

Fig. 4. Photoluminescence spectra of CZTS films electrodeposited at different times.

4. Conclusion

In summary, we have reported the deposition time effect on CZTS thin films obtained by single step electrochemical deposition followed by a sulfurization treatment at 500°C for 80 min under Argon atmosphere. All the films showed the distinct diffraction peaks of the single pure phase of the kesterite structure. EDS study revealed that the sample deposited at 30 min was nearly stoichiometric, being Cu-deficient and Zn-rich in composition which is suited to the solar cell applications. Increasing the deposition time to 30 min, the surface morphology became more homogeneous and compact. PL measurements demonstrated that the band gap energies of all deposited samples were found to be around 1.45 eV.

Acknowledgments

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 608593 (EUROSUNMED Project).
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