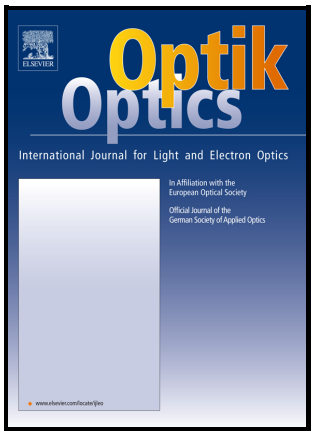

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PII: S0030-4026(21)01835-0

DOI: https://doi.org/10.1016/j.ijleo.2021.168320

Reference: IJLEO168320

To appear in: *Optik*

Received date: 19 July 2021
Revised date: 8 November 2021
Accepted date: 9 November 2021

Please cite this article as: S. AZMI, O.AIT LAYACHI, M.E. OUARDI, E.M. KHOUMRI, A. MOUJIB, A.E. BROUZI, M. NOHAIR, L. PEZZATO and M. DABALA, Growth of Cu_2ZnSnS_4 Thin Film Absorber Layer on Transparent Conductive Oxides and Molybdenum Substrates by Electrodeposition for Photovoltaic Application, *Optik*, (2021) doi:https://doi.org/10.1016/j.ijleo.2021.168320

Growth of Cu_2ZnSnS_4 Thin Film Absorber Layer on Transparent Conductive Oxides and Molybdenum Substrates by Electrodeposition for Photovoltaic Application

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Abstract

Cu_2ZnSnS_4 (CZTS) absorber layer for the photovoltaic application was successfully deposited on different substrates, indium tin oxide (ITO), fluorine-doped tin oxide (FTO) and molybdenum (Mo) using a single step electrodeposition process. The structural, morphological and optical properties of the CZTS films were analyzed by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), and photoluminescence (PL). The present study was designed to determine the effect of the substrate on the kesterite thin film properties grown by electrodeposition. The results confirm that the CZTS properties depend on the substrate nature. Furthermore, the CZTS films deposited on Mo substrate was found more appropriate for CZTS based solar cells due to their crystallinity and good morphology as well as their suitable energy bandgap around 1.6 eV.

Keywords

Cu_2ZnSnS_4, Solar Absorber Layer, Thin Film Photovoltaics, Electrodeposition, Molybdenum, Transparent Conductive Oxides

1. Introduction

The $Cu_2ZnSn(S,Se)_4$ polycrystalline kesterite solar cell (CZTS) is a p-type semiconductor with an absorption coefficient around 10^{-4} cm^{-1} and bandgap energy close to 1.6 eV [1]. Kesterite is essential for a wide range of solar cells technologies owing to the abundance of its components and its low production cost [2].

Furthermore, CZTS thin film solar cells are of interest because they reached remarkable conversion efficiencies up to 12.7% [3]. For the development of these thin layers, several techniques have been reported, including vacuum and non-vacuum based deposition processes. The adoption of vacuum-based technologies such as pulsed laser deposition [4], sputtering [5], thermal evaporation [6], and electron beam evaporation [7] increases manufacturing costs. The use of solution-based deposition approaches, such as sol-gel [8], spin coating [9], spray pyrolysis [10], successive ionic layer adsorption and reaction (SILAR) [11], screen printing [12] and electrodeposition [13] decreases the manufacturing costs. Recent developments in electrodeposition have heightened the need for producing high efficiency materials using low cost and environmentally friendly processes. Therefore, among the cited techniques, the electrochemical process presents several advantages, to be inexpensive, easy to develop and may allow large-scale semiconductor deposition and low cost industrial production [14].

The electrodeposition of the CZTS absorber layer route can be achieved using one step [14, 15] or two steps [16]. Over the past decade, most research in CZTS (Se) based solar cells have emphasized the use of Mo substrate, it has significant benefits in terms of having good thermal stability and an ohmic contact with CZTS(Se) [17]. However, the opaque property of the Mo substrate limits its use as a back contact for semi-transparent materials, and tandem solar cells [17]. Therefore, the emergence of transparent conductive oxides (TCO) as secondary contact can expand the application of the CZTS absorber layer and provide new applications as transparent solar cells [19]. Regarding the kesterite-based solar cells, only a few studies reported the use of TCOs as back contact [18-21]. The most commonly used TCOs are based on tin-doped indium oxide (In_2O_3: Sn, ITO), or fluorine tin-doped oxide (SnO_2: F, FTO). The best-reported efficiencies reached using these back contact is 5.8% with indium tin oxide ITO coated glass as a back contact for CZTS solar cells [22]. It is reported that this low efficiencies results from an interfacial reaction at the back contact of the ITO, which induces the indium diffusion in the CZTS(Se) absorber and the creation of a thin layer of SnO_x oxide, thus degrading the back interface of the CZTS(Se) [20].

This study aims to compare the properties of CZTS thin film deposited by one-step electrodeposition using three glass different substrates TCOs: ITO, FTO and Mo coated glass. The novelty of this paper is related to the investigation of the chemical,

morphological and optical properties of the kesterite CZTS thin film prepared on the different substrates by electrodeposition for photovoltaic application. Thus, the methodology used in this work consists of one-step electrodeposition of quaternary Cu-Zn-Sn-S from one bath followed by an annealing treatment, since all constituents are provided from the same electrolyte; it is attractive in further reducing the thin film manufacturing cost. However, the electrodeposition process is governed by several parameters that have to be optimized in order to obtain CZTS thin film with suitable properties. Based on our previously published works [2,13,23] related to the optimization of the electrodeposition synthesis route; the application of -1.1V vs SCE for 30 min was found to be the optimum deposition condition, and 450 °C was fixed as the best annealing temperature leading to a pure CZTS kesterite phase obtention. For this study, it was of interest to investigate a comparative study to highlight the effect of the substrate on the morphological, crystallographic and optical properties of CZTS thin film elaborated by electrodeposition.

2. Experimental details

Electrodeposition of Cu-Zn-Sn-S thin films onto Molybdenum (Mo), ITO and FTO coated glass substrates was performed using a three electrodes electrochemical cell system composed of Mo, ITO, FTO as working electrodes (WE), Saturated Calomel Electrode (SCE) as a Reference Electrode (RE) and platinum wire (Pt) as a Counter Electrode (CE). The potentiostat/galvanostat AUTOLAB (Metrohm-Autolab, Utrecht Netherlands) PGSTAT302N controlled by GPES and FRA software version 4.9 were used to control the three electrodes system and to study the electrochemical behaviour of the samples. The working electrodes were ultrasonically pretreated using acetone, ethanol and distilled water for 15 min, and then dried under N_2 flow. The thin films have been prepared by electrodeposition from an aqueous solution obtained by dissolution of analytical grade reagents of zinc sulfate (20mM), copper sulfate (5mM), tin chloride (10mM), and sodium thiosulfate (20mM) in citric acid ($C_6H_8O_7$) (0.1M). Tartaric acid ($C_4H_6O_6$) was added to reach a pH value between 4 - 4.5 and trisodium citrate ($Na_3C_6H_5O_7$) was used as a complexing.

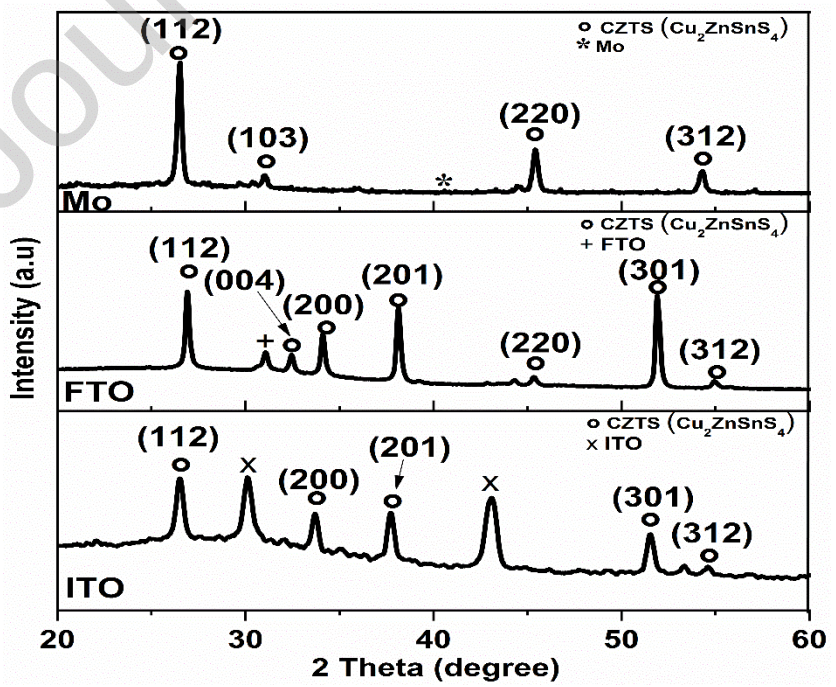
The cyclic voltammetry study was used to determine the electrodeposition range of CZTS. The CZTS samples were elaborated using a single step electrochemical process in potentiostatic mode, applying the optimum potential for each working

electrode at the range of -1.1V with respect to the SCE electrode at room temperature without stirring. Therefore, the as deposited films were annealed at 450 °C for 30 min. Based on the previously reported study on the effect of annealing treatment on CZTS kesterite film synthesized on Mo and TCO substrates [2], 450°C is the optimum temperature range leading to a nearly stoichiometric pure kesterite phase with the best optical band gap. The crystalline structure of CZTS thin films was characterized using Siemens D500 X-ray diffractometer (Siemens, Munich, Germany) with a Ni-filtered Cu-Kα radiation source (λ= 0.15405 nm) and confirmed by Thermo Scientific™ DXR™3 Raman Microscope in the backscattering geometry with a λ = 514 nm and Ar laser as an excitation. Surface morphology of the samples was observed by Hitachi SU-70 Field Emission Gun Scanning Electron Microscope (SEM). The photoluminescence (PL) spectra were recorded at room temperature using a FluoroMax 4P spectrophotometer

3. Results and discussion

3.1 X-ray diffraction measurements (XRD)

The crystal structure of CZTS samples was examined using XRD analysis. The structural properties of the CZTS thin films deposited by one-step electrodeposition on ITO, FTO and Mo substrates are displayed in figure 1. The patterns were recorded in a 2Θ angle range of 20°-60°. The presence of multiple



peaks in the XRD patterns confirms the films polycrystalline nature [25].

Figure 1: *XRD analysis of CZTS thin films growth on different substrates: a) Mo b) FTO and c) ITO*

The film prepared using FTO, ITO and Mo substrates exhibits principal X-Ray diffraction peaks corresponding to the (112) and (312) planes of a single kesterite-type CZTS structure (JCPDS No.: 26-0575).

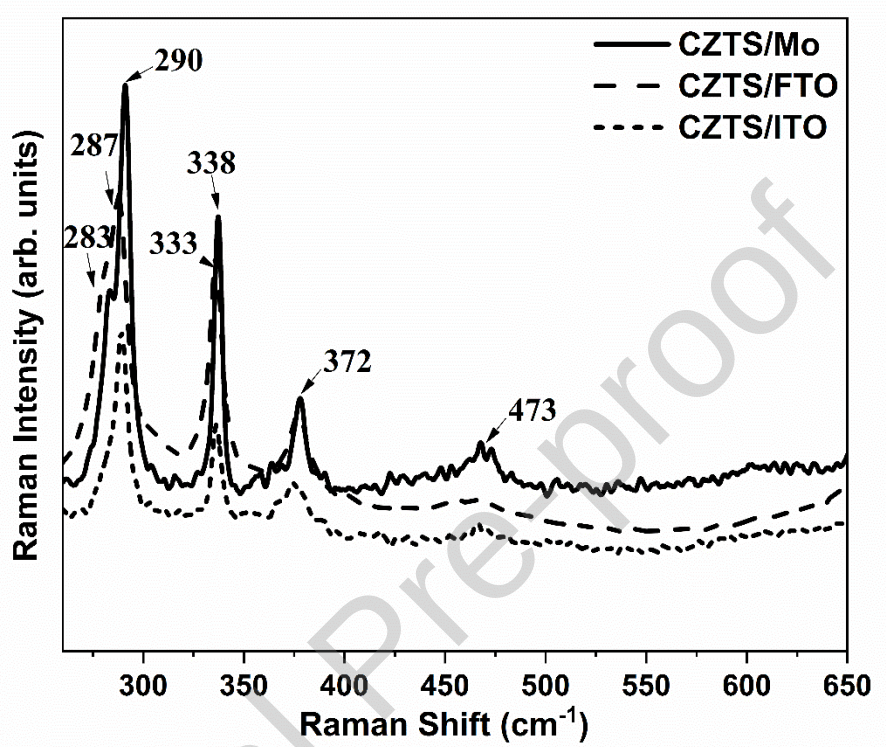
The diffraction peak positions in the ITO and FTO samples are almost similar; the major peaks at ~ 47°, ~ 34°, ~ 38°, and ~ 52° correspond to the (220), (200), (201) and (301) planes of CZTS, respectively. The similarity of the XRD patterns of the CZTS elaborated on ITO and FTO coated glass is due to their common physicochemical properties. Regarding the Mo sample, an additional peak is observed at ~ 52° connected to the CZTS kesterite (103) plane. By comparing the three samples, it is observed that the intensity of reflection (112) for the Mo sample is bigger compared to the TCO samples (FTO and ITO), suggesting an increment in grain size compared to the other substrates [38]. The advantageous crystalline property of the CZTS film prepared on Mo could be related to the thermal stability of the Mo based substrate compared to the TCO based substrate. Furthermore, it can be seen from figure 1 that the peaks corresponding to the film secondary phase are absent from all the diffraction patterns. This confirmed that the prepared thin films present a kesterite single-phase.

3.2 Raman Spectroscopy

In the Kesterite field, the X-ray diffraction analysis is not sufficient to confirm the presence of CZTS pure phase without apparition of secondary phases due to indistinguishable peak positions of Cu_2ZnSnS_4, Cu_2SnS_3 and ZnS in an X-ray diffractogram. Therefore, Raman spectroscopy was investigated and the results are presented in figure 2. Basing on the Raman spectra recorded from 260 cm^{-1} to 650 cm^{-1} ranges, the film synthesized using FTO, ITO and Mo display spectra with principal peaks recorded at 287 cm^{-1}, 333-338 cm^{-1}, and 372 cm^{-1} correspond to kesterite CZTS phases as reported [26-29,39].

The CZTS films synthesized on Mo and FTO display other kesterite CZTS peaks at ~ 283 cm^{-1} and 473 cm^{-1}, which are in agreement with the previous report [30,40]. However, the difference in peaks intensity is well observed and could be related to different reasons. In this study, the intensity enhancement could be related

to the crystallinity increases since the CZTS kesterite belongs to a single crystalline lattice [31], therefore, CZTS film synthesized on Mo substrate displays the best crystalline form which is in accordance with x-ray diffraction results. Furthermore, the Raman spectra recorded for the Mo sample present a slight shift in the peak



position compared to the FTO and ITO samples, this phenomenon could be perhaps related to the growth of the MoS_2 interfacial layer which causes an ohmic behaviour and prominently affects the preferred orientation of CZTS kesterite [41].

Figure 2: *Raman spectra of CZTS deposited on different substrates Mo, FTO, and ITO at 532 nm*

3.3 Morphology Properties

The surface morphology of films prepared on ITO, FTO and Mo substrates was investigated using scanning electron microscopy (SEM) and the results are shown in figure 3. The obtained micrograms display a uniform morphology without the presence of cracks and pinholes. Morphological study for all the samples demonstrates the agglomeration of particles, which allows prevention recombination, which is one of the preferred characteristics for solar cell applications [32]. However, the morphology of the grains depends on the substrate nature. The CZTS film growth on ITO coated glass shows a distribution of small particles in the entire surface of the

substrate leading to a compact and homogenous layer of CZTS deposited on ITO as shown in Figure 3 (a and b). The films deposited on the FTO substrate presents agglomerated crystals grouped to form large and compact clusters like a cauliflower around 300 nm in size as shown in figure 3 (c and d). From figure 3 (e and f), we noticed that CZTS deposited on Mo substrate demonstrates a small particle clustered and formed bigger agglomerations distributed in all the areas as it is shown clearly in figure 3 (e).

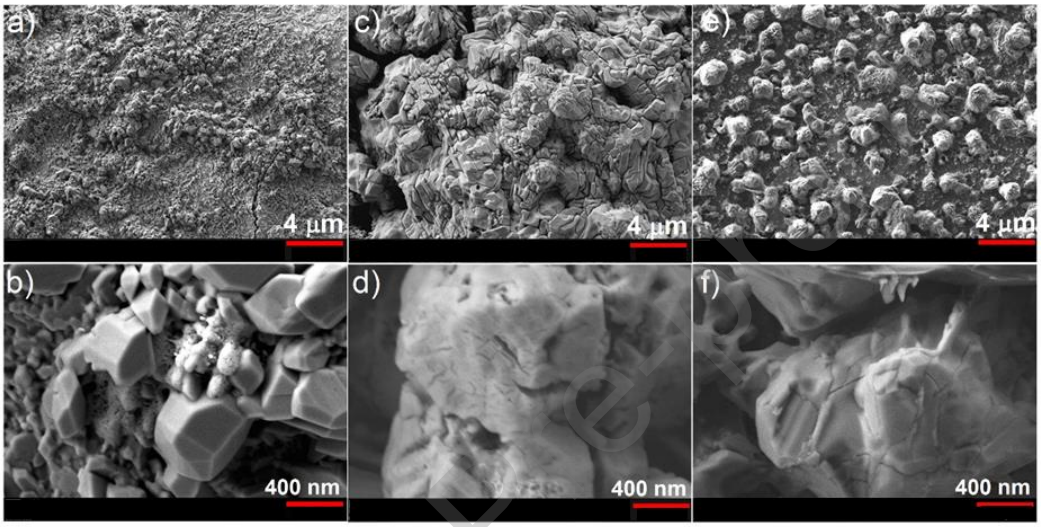


Figure 3: *SEM images of deposited CZTS thin films using (a) and (b) ITO, (c) and (d) FTO and (e) and (f) Mo substrate.*

Furthermore, it can be seen that the CZTS film deposited on ITO substrate (figure 3 (a)) has the smallest kesterite grain size compared to the films synthesized on FTO and Mo substrates. Furthermore, the CZTS films deposited on Mo substrate presents a bigger kesterite grain size as shown in figure 3 (e). Despite using the same experimental conditions to grow CZTS thin film on FTO, ITO and Mo, the CZTS growth morphology is different. This could be probably related to the effect of the used substrate on the process growth; On the one hand, for the CZTS/Mo, the presence of MoS_2 interlayer affects the crystalline orientation of the CZTS which explain the difference in the morphology. On the other hand, tin (Sn) is one of the component elements of the ITO substrate and its presence can change the elaboration process of the kesterite film.

3.4 Optical Properties

In order to study the physical properties of the CZTS thin film elaborated by one-step electrodeposition on different substrates, the photoluminescence (PL)

analysis was investigated. Figure 4 shows a plot of CZTS thin film synthesized on Mo, ITO, and FTO photoluminescence spectra. The room temperature photoluminescence (PL) spectra of CZTS thin film samples presents broadband peaking at different values, around 717 nm (1.72 eV), 731 nm (1.69 eV) and 793 nm (1.53 eV) for the CZTS film elaborated on ITO, FTO and Mo substrates, respectively. As the excitation wavelength is above the optical bandgap of the CZTS thin film (from 1.2eV [34] to 1.8 eV [35]) the luminescence was tentatively assigned to band-to-band recombination [36].

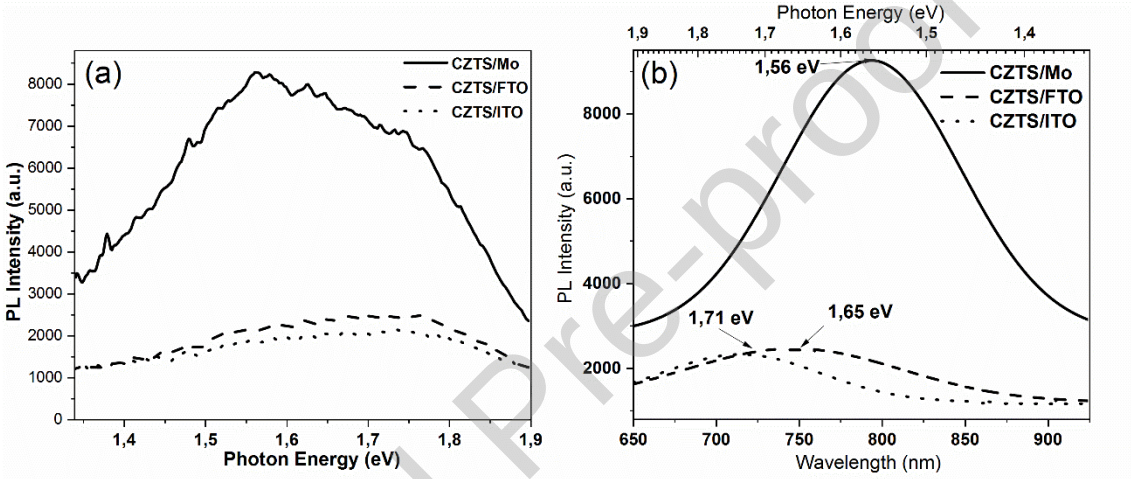


Figure 4: *(a) photoluminescence (PL) of Cu_2ZnSnS_4 thin film synthesized on different substrates under 515 nm (2.4m eV) excitation wavelength*; *(b) Deconvolution of the PL curve recorded on samples by using Gaussian shape curves.*

The photoluminescence spectra of the film elaborated on FTO and ITO substrates does not present a remarkable shift and difference in term of PL intensity and bandgap energy. Furthermore, the photoluminescence signal recorded for CZTS thin film prepared on Mo substrate presents the lower value of bandgap energy (1.6 eV), which may be attributed to the crystalline size and morphological properties of the CZTS/Mo sample as illustrated from the SEM investigation (fig. 3(e)), because the biggest crystalline agglomerations increases the possibility of light scattering within the respective film depletion zones and increase the absorption of light within the cell [33, 37,]. However, the bandgap strongly depends on the particle size and the presence of the secondary phases. Basing on the PL results, the bandgap of the CZTS films deposited on Mo substrate makes it suitable for photovoltaic application compared to the other substrates.

4. Conclusion

In this investigation, the aim was to assess CZTS thin films deposited using single step electrodeposition on Mo, ITO and FTO coated substrate. The thin films were studied using several surface characterization techniques to confirm the kesterite phase presence. The X-ray diffraction and Raman spectroscopy confirm the crystallinity increase of the films prepared on Mo coated glass compared to the film prepared on the transparent oxide substrates. It is seen from the SEM micrographs that the film prepared on Mo presents a larger grain size with a uniform distribution. The bandgap energy of the films was found 1.56, 1.69, 1.71 eV for Mo, FTO and Mo, respectively. It could be concluded that the structural and physical properties of CZTS films depend on the substrate nature. Mo coated glass was found to be the optimum substrate for CZTS thin film electrodeposition which presents the best surface properties to be employed as a back contact for photovoltaic application.

Acknowledgements

All authors acknowledge the financial support from the Moroccan Ministry of Higher Education and Research and CNRST.

Conflicts of interest or competing interests

The authors declare that they have no conflict of interest.

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Declaration of Competing Interest

☒ The authors declare that they have no known competing financial interests or personal relationships
that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered
as potential competing interests: