



Deposition of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) prepared by a solution route for solar cells applications

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Received 2014, Revised 14 March 2015, Accepted 14 March 2015

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Abstract

As a promising candidate as absorber layer in thin film solar cells, the $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) material has gained a broad interest over recent years for the production of low-cost solar cells due to its direct and tunable band gap energy, high optical absorption coefficients and also due to the abundance and the non-toxicity of all its constituents. In addition, to solve the problem of expensive and complicated vacuum-based synthesis methods, simple and low-cost methods have been developed for the preparation of this material. In this present work, the CZTS thin films have been prepared using a solution route namely sol-gel, which is a simple and low cost method for a large production of thin films materials and spin coated onto glass substrates. The sol-gel precursor solution was made from metal salts of copper (II) chloride (CuCl_2), zinc (II) chloride (ZnCl_2), Tin (IV) chloride (SnCl_4), and thiourea ($\text{CS}(\text{NH}_2)_2$) dissolved into a mixture of ethanol/water as solvent. The X-ray diffraction studies showed the formation of a kesterite structure with peaks corresponding to (112) and (220) directions. The Raman spectrum indicated the presence of the principal kesterite peak at 336 cm^{-1} and the existence of a strange peak at 424 cm^{-1} which could be attributed to the binary compound Cu_2S . The absorbance spectrum has been recorded for the estimation of the band gap. The CZTS thin film can be made using a simple spin coating technique, but improvements in the film properties by a suitable annealing time and temperature as well as annealing environment and post deposition needs have to be done for making a quality photovoltaic absorber.

Keywords: $\text{Cu}_2\text{ZnSnS}_4$, sol-gel, spin coating, photovoltaic absorber material, characterization.

1. Introduction

Energy demand is increasing following the development of industry, transportation and growth worldwide [1]. To meet the ever increasing demand for energy and to cope with the limited fossil resources available, photovoltaic solar energy production will become increasingly important. In order to reduce the cost of solar cells, new alternative materials in thin films have been investigated by researchers during recent years for the development of next generation of efficient and cost-effective solar cells. Among them Copper Indium Gallium Diselenide (CIGS) and Cadmium Telluride (CdTe) have been successfully synthesized and have reached the commercialization stage [2-6]. However, the scarcity and toxicity of some elements such as Indium, Cadmium and Selenide could be a brake to the development of solar cells based on these materials. To develop new PV materials constituted of abundant elements in nature and which are cost-effective and eco-friendly is therefore an important and necessary issue to overcome the problem of limitation. In this context, Copper Zinc Tin Sulfide

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) has emerged as one of the promising and alternative candidates to CIGS and CdTe for low cost and sustainable solar cells due to its p-type conductivity, its good optoelectronic properties and also due to the non toxicity and the availability of all its constituents in the earth crust [7-9]. It is a suitable material for solar energy conversion with a near optimal direct band gap ranging from 1.4 to 1.6 eV and high optical coefficient ($\geq 10^4 \text{ cm}^{-1}$) [10, 11]. The conversion efficiency of CZTS-based solar cells has been improved from 6.7% in 2008 to 12.6% in 2014 [12, 13]. Several deposition techniques have been used for CZTS thin film manufacture, such as pulsed laser deposition [14], co-sputtering [15], thermal evaporation [16], electrodeposition [17], sol-gel [18], spray pyrolysis [19,20], etc...

In this work, we report the synthesis of CZTS thin film, by spin coating technique, on ordinary glass substrate. By this low cost process, the CZTS absorber layer could be prepared easily which may be useful for photovoltaic applications and may reduce the cost of solar cells.

2-Experimental details

$\text{Cu}_2\text{ZnSnS}_4$ thin films were deposited by spin coating technique starting with a solution containing copper (II) chloride (CuCl_2) (1.8M), zinc (II) chloride (ZnCl_2) (1.1M), Tin (IV) chloride (SnCl_4) (1M), and thiourea ($\text{CS}(\text{NH}_2)_2$) (7.4M), as source of sulfur dissolved into a mixture of ethanol/water (30:70) as solvent. A clear yellow solution was formed directly after adding of thiourea and was stirred for half an hour at 40°C to ensure that all metal salts have been dissolved completely. To prepare thin films, this solution was spin-coated onto ordinary glass substrates which were previously cleaned into acetone, distilled water and ethanol at 2500 rpm for 30s followed by a solvent drying at 110°C for 10min on a hot plate. The spin-coating and drying processes were repeated 3 times to have a suitable thickness of the film. Finally, the annealing temperature was elevated to 350°C during 15 min for growing polycrystalline CZTS thin films in air atmosphere. We have investigated the structural, morphological and optical properties of the films. X-ray diffractometer and Raman spectroscope were used to record X-ray diffraction (XRD) pattern and Raman spectrum of the films in order to examine their crystalline structure. The spectral transmittance of the film was recorded in the wavelength range 400-2500 nm by using a VIS-IR spectrophotometer. The microstructure and the surface morphology were observed using a scanning electron microscope (SEM). The elemental composition was determined using energy dispersive spectrometer (EDS) system connected to the SEM.

3- Results and discussion

3.1) Structural and Morphological Properties

Figure 1a shows the XRD pattern for the film annealed at 350°C for 15min. The film is of polycrystalline type showing peaks located at 28.3° and 47.5° corresponding to the (112) and (220) directions.

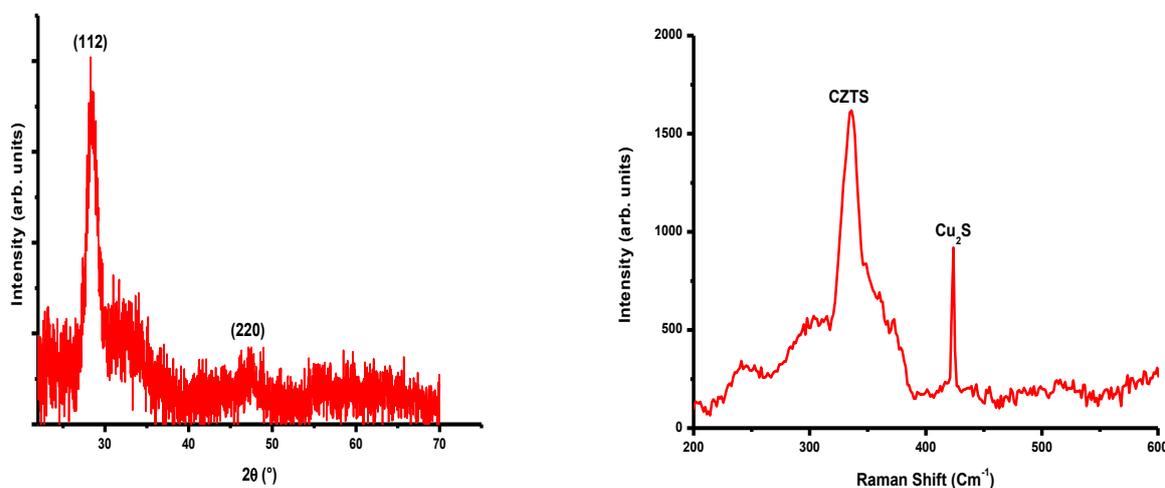


Figure1 : XRD pattern (a) and Raman spectrum (b)

The film shows also a preferential direction along (112) which is characteristic of a kesterite structure. The low intensity of these peaks can be attributed to the short annealing time since the time has not been sufficient to allow the compound to grow completely. The Raman spectroscopy was used to obtain further insight into the phase identification, the result is shown in *Figure 1b*. The synthesized film exhibits a peak at the position 336 cm^{-1} which corresponds to a kesterite structure and we can say that the Raman spectroscopy confirms the XRD pattern. Hence both XRD and Raman spectrum confirm well the formation of a CZTS thin film. Moreover, we can see a peak located at 424 cm^{-1} which may correspond to the binary phase Cu_2S due certainly to the sulfur deficient occurring during different steps of the synthesis [21, 22].

SEM image of CZTS film is shown in *Figure 2* which indicates that the film has uniform surface features over the entire area.

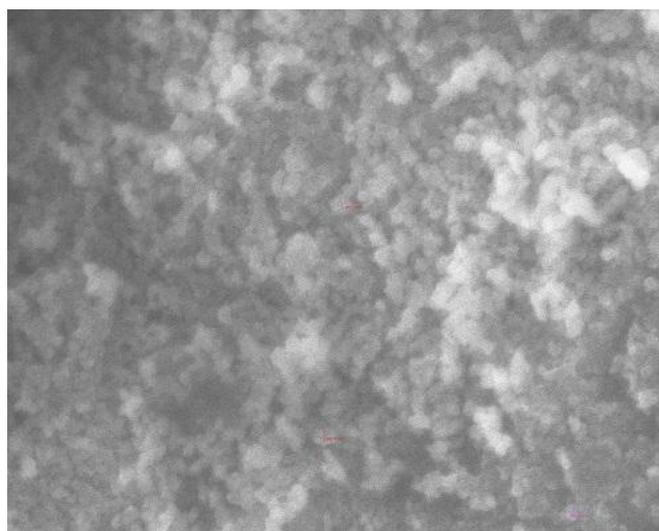


Figure 2: Surface morphology of the CZTS thin film

The EDX results shown in *Table 1* confirm proper elemental composition of the synthesized film. Sulfurization/selenization treatment as well as a suitable annealing time will be needed to achieve improvements in the compositional and structural properties.

Table 1: Elemental composition of the spin-coated CZTS film

Element	Elemental composition (%)
Cu	32.32
Zn	13.96
Sn	34.50
S	19.22

3.2) Optical properties

The optical properties of the synthesized film have been carried out through the measurement of the absorbance spectrum and the optical band gap was estimated by the absorption spectrum fitting (ASF) method [23]. It is possible to determine the energy band gap in semi-conductors that only requires the measurement of the absorbance spectrum without any information on film thickness or reflectance [24, 25]. This can be done by the method so-called absorption spectrum fitting (ASF) [23]. This method suggests that finding the wavelength λg corresponding to the optical band gap by extrapolating the linear part of $\left(\frac{Abs}{\lambda}\right)^2$ vs. $\frac{1}{\lambda}$ curve at $\left(\frac{Abs}{\lambda}\right)^2 = 0$ and to

use the relation $E_g = 1239.83/\lambda_g$ to evaluate the band gap; Abs, E_g , λ_g are the absorbance, the band gap and the wavelength corresponding to the band gap respectively. More details can be found in [23]. We have used this method since we have not been able to measure the thickness of our film.

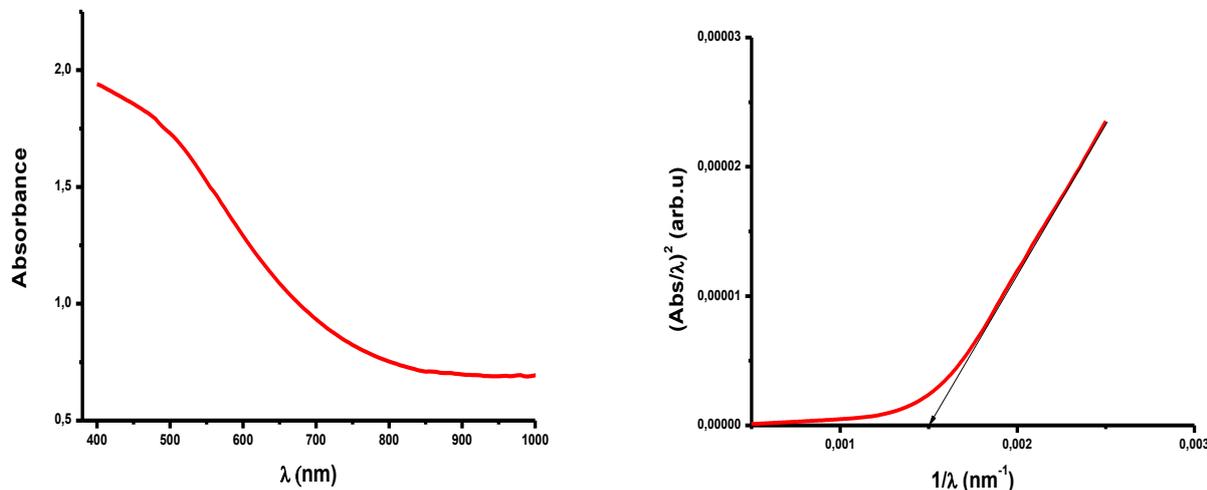


Figure 3: Absorbance (a) and ASF plot (b) of CZTS thin film deposited by spin coating

Extrapolating the straight-line portion of the plot shown in *Figure 3b* to the zero $\left(\frac{Abs}{\lambda}\right)^2$ gives the corresponding value of E_g (eV). A band gap of 1.87 eV has been obtained for the film annealed in air which is outside of the optimal range of the CZTS band gap namely 1.4-1.6 eV [10, 11]. The high band gap may be attributed to the residual organic precursor compounds of the sample at relatively low annealing time and temperature. It can be due also to the presence of the binary compound Cu_xS which has a direct optical band gap ranging from 1.7 to 2.16 eV for x varying from 1 to 2 [26, 27]. At relatively low annealing time, the compound can be well present but surrounded by many impurities and the high band gap may be due to the presence of one or many of these impurities. We can attribute also the high band gap to the annealing environment which is not suitable to keep all the elements of the compound in a stoichiometric proportion. Pawar et al [28] reported that the band gap of CZTS thin film is 2.7eV before annealing in various atmospheres such as Ar, N_2 , N_2+H_2S and is find to be in the range of 1.48-1.7eV after an annealing in these gases. Hence one of the main conditions to synthesize the CZTS compound using a solution route with good optical properties is to have a suitable annealing environment, as well as a suitable annealing temperature and time.

Conclusion

Cu_2ZnSnS_4 thin films have been synthesized by the sol-gel method and spin coated on ordinary glass substrates. The annealing was done in air. The XRD spectrum indicates that the film obtained is polycrystalline belonging to a kesterite structure with preferred orientation along the (112) direction. The Raman spectroscopy shows the appearance the binary phase Cu_2S due to the evaporation of sulfur during stirring, drying and annealing processes. A band gap of $E_g = 1.87$ eV has been obtained from optical measurements. This value of energy gap could be improved by annealing the films in environments different from air, such as Argon, Nitrogen, Sulfur or nitrogen-sulfur both atmosphere to avoid also the risk of oxidation.

Acknowledgments: Joel. H. N. Tchognia is grateful to the ICTP (*The Abdus Salam International Centre for Theoretical Physics*) and ANSOLE (*African Network for Solar Energy*) for financial support in the framework of the Intra-African Exchange (INEX) program. The authors thank researchers from LMOPS (Metz, France), IES (Montpellier, France) and GOPS (Valencia, Spain) laboratories for their help during the stay of ANEPMAER researchers.

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(2015) ; <http://www.jmaterenvirosnci.com>