

Effect of substrate temperature on physical properties of CZTS thin films

Y. ARBA*, M. RAFI, H. TCHOGNIA, B. HARTITI, A. RIDAH, P. THEVENIN^a

LPMAER Laboratory, Department of Physics, University Hassan II FSTM, Mohammedia, Morocco

^aLMOPS Laboratory, University of Lorraine, Metz, France

Copper zinc tin sulfide ($\text{Cu}_2\text{ZnSnS}_4$, CZTS) thin films have been deposited using spray pyrolysis technique on glass substrates at temperatures from 350°C to 425°C by step of 25°C. The structural, morphological and optical properties of as-deposited films have been studied using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Raman Spectroscopy measurements. SEM studies revealed that the CZTS films exhibited uniformly distributed grains over the entire surface of the substrate. The analysis of XRD revealed that all CZTS thin films are of polycrystalline type belonging to the kesterite structure with a preferential orientation along the [112] axis. The best crystallinity of CZTS thin films has been obtained for the substrate temperature 375°C. The optical measurement shows a band gap energy of 1.57eV for this substrate temperature which is quite close to the optimum band gap energy for thin film solar cells.

(Received September 28, 2013; accepted November 7, 2013)

Keywords: Spray Pyrolysis, $\text{Cu}_2\text{ZnSnS}_4$, Solar cell, Absorber, Characterization

1. Introduction

Thin film solar cells based on polycrystalline CdTe, CIS, and CIGS have reached the commercialization stage. However, restrictions on heavy metal usage for Cadmium and limitations because of its scarcity and mainly due to its high cost for Indium and Tellurium have raised concern about limitations on production capacity of the photovoltaic devices [1]. To solve this issue, it is necessary to develop alternative absorber materials that are both non toxic and easily available. In this context, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) quaternary material has emerged as one of the promising candidates due to its tunable direct band gap energy around 1.5 eV and its large absorption coefficient ($>10^4 \text{ Cm}^{-1}$) [2]. All the components in CZTS are earth abundant and environment benign. The abundance of Cu, Zn, Sn, and S in the earth crust are 55, 70, 20, and 260 ppm, respectively [3]. CZTS is a mineral material which shares a similar structure with the chalcopyrite CIS, except that half of the Indium is replaced with Zinc and another half with Tin [4]. According to the Shockley-Queisser limit, CZTS solar cells are expected to have theoretical conversion efficiency in excess of 30% [5]. Several deposition techniques have been used for CZTS thin films synthesis. Thermal evaporation was tested by T. Friedlmeier et al. [6]. E-Beam evaporation with post sulfurization process was studied by Katagiri et al. [7]. K. Jimbo et al. were successful in growing CZTS using RF co-sputtering of binary compounds [8]. Routes using co-evaporated elements were developed by T. Tanaka et al. [9]. Non vacuum methods have also been developed namely sulfurization of sol-gel deposited precursors by K. Tanaka et al. and spray-pyrolysis by N. Nakayama et al. and N. Kamoun et al. [2, 10 and 11].

In this work, we have synthesized and studied the temperature dependence on the structural, morphological and optical properties of CZTS as an absorber material in thin films solar cells. CZTS thin films were synthesized using a solution route and deposited on glass substrates at various temperatures by Spray Pyrolysis technique. The starting precursors containing ions of copper, zinc, tin and sulfur were dissolved in an aqueous bath. The structural characterization of synthesized films was analyzed using the X-ray diffraction (XRD). The morphological study of as-deposited thin films was carried out by scanning electron microscopy (SEM). The optical properties of CZTS thin films were also investigated.

2. Experimental

The $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films were synthesized by spray pyrolysis technique starting with an aqueous solution containing cupric chloride (0.01M), zinc acetate (0.005M), stannic chloride (0.005M) and thiourea (0.04M). An amount of thiourea was added to compensate the loss of sulphur during pyrolysis. The precursor solution was sprayed, using a pneumatically controlled air-atomizing spray nozzle (14JAU, Spraying systems Co., USA), onto heated glass substrates held at various substrate temperatures. Compressed air was used as the carrier gas; the spray rate and the spray duration were 1ml/min and 60min respectively. Experiments were conducted at various substrate temperatures in the range of 350°C-425°C by step of 25°C to investigate their effect on the growth of the films.

3. Results and discussion

3.1 Structural properties (XRD)

Fig.1 shows the X-ray diffraction spectra for CZTS thin films deposited at different temperatures. For all the as-deposited films, we can see some peaks at around $2\theta = 28.08^\circ$, 32.32° , 46.57° and 55.28° corresponding to the (112), (200), (105) and (312) planes of CZTS respectively, which are characteristic of the kesterite structure. A preferential (112) orientation was observed for all deposited films. Moreover, we can see some peaks corresponding to the binary phase (Cu_2S) [12-13]. So the crystallization of CZTS cannot be confirmed solely by XRD analysis. This could be completed by Raman scanning measurements. The study of X-Ray Diffraction measurements indicates that the films synthesized at the temperature of 375°C exhibit the best crystallinity with a sharp peak located at 28.08° .

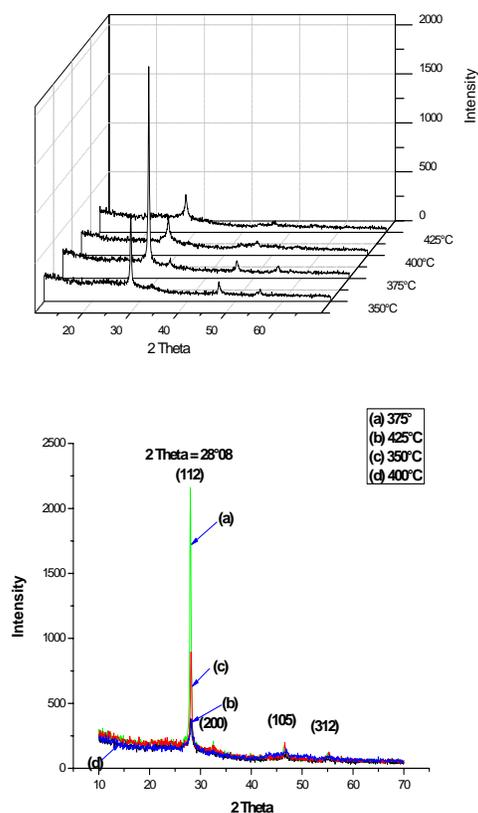


Fig.1. XRD patterns of CZTS samples prepared at different temperatures.

3.2 Microstructure (SEM)

In Fig. 2, we can see the SEM images of samples elaborated at 350°C , 375°C , 400°C , and 425°C . For all the as-deposited films, one can see nanocrystals with densely

packed grains distributed evenly throughout the entire surface of the film. The grain size increases with increasing the substrate temperature. It should be noted that significant porosity is developed at high temperatures (above 375°C). This may indicate that larger grains and/or high temperature conditions may be more susceptible to evaporation of CZTS or some of its components (sulfur), especially from grain boundaries. These images show clearly a compact and homogenous surface for temperatures less than 400°C and cracked surface at temperatures above 375°C . For sample prepared at 375°C , there is an increase in nucleation over growth and one can see a uniformly smooth structure, homogenous with condensed grains.

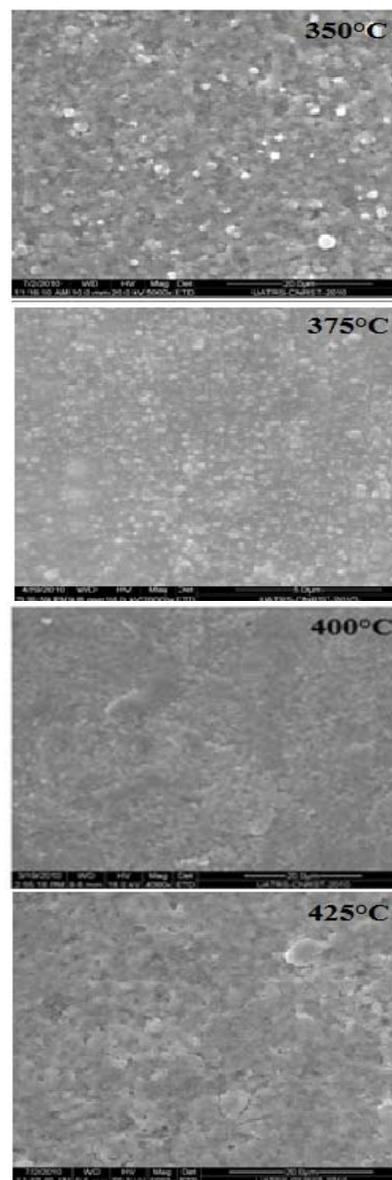


Fig.2. SEM images of samples prepared at different elaboration temperatures

3.3 Raman spectroscopy

The Raman spectroscopy was utilized to obtain further insight into phase identification, and the results of the CZTS films as a function of substrate temperatures are shown in Fig.3. The as-prepared precursor films exhibited a peak at 473 cm^{-1} which correspond to the binary phase Cu_{2-x}S comparable with the results of X-ray diffraction (Fig.1) and published by other research works [14,15]. This undesirable phase may disappear by annealing the films in a sulfurized atmosphere to compensate the evaporated sulfur or by a KCN treatment [16,17]. Raman analysis indicates that the crystallization of CZTS increases with substrate temperature up to the value of 375°C and the CZTS quaternary phase is more significant than the binary Cu_{2-x}S . The inverse phenomenon occurs at high temperatures where one can see better the formation of binary phase and the disappearance of the quaternary CZTS phase due certainly to the loss of sulfur. For sample elaborated at the substrate temperature of 375°C , we can see a strong peak at 332 cm^{-1} , resolute with a good quality signal to noise which shows a good crystallization of CZTS at this temperature confirmed by XRD and SEM analysis.

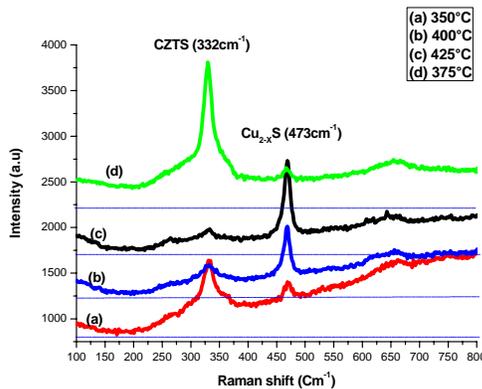


Fig. 3. Raman spectra of thin CZTS for $T = 350^\circ\text{C}$, 375°C , 400°C and 425°C .

3.4 Optical properties

The optical absorption data was analyzed using the following classical relation of optical absorption in a semiconductor:

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu}$$

Where A is a constant, E_g the band gap, $h\nu$ the photon energy and $1/2$ a constant corresponding to the direct allowed transition between bottom of the conduction band and top of the valence band.

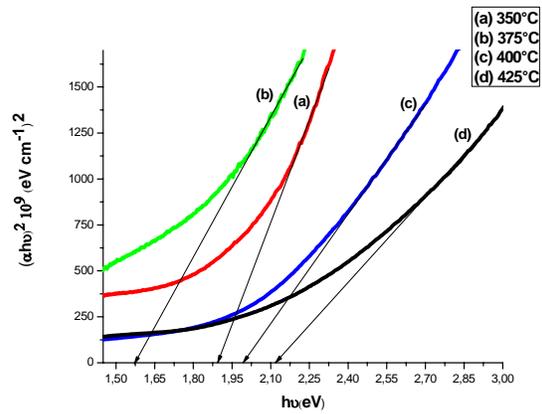


Fig.4 Variation of $(\alpha h\nu)^2$ with the incident photon energy from the transmission for samples prepared at different temperatures.

Fig. 4 shows the variation of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) for as-deposited CZTS thin films at different elaboration temperatures. Based on the direct allowed inter band transition theory, the optical band gap of CZTS is determine by extrapolating the linear part of the curve to the zero absorption coefficient ($\alpha = 0$) as shown in Fig.4. The band gap of the as-deposited CZTS thin films is found to be 1.89eV, 1.57eV, 1.99eV, and 2.12eV for elaboration temperatures of 350°C , 375°C , 400°C , and 425°C respectively. The sample deposited at the substrate temperature of 375°C exhibits a band gap similar to the band gap of bulk CZTS in comparison with those reported by others (1.56 and 1.54 eV respectively) [16, 18] and is quite close to the optimum band gap energy for thin film solar cells. In contrast, for samples elaborated at other substrate temperatures the band gap values of the CZTS films increase from 1.89eV to 2.12eV. This increase might be due to the presence of Cu_2S , which has the direct optical band gap in the range 1.7eV-2.16eV [19, 20].

4. Conclusions

The $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films were deposited by chemical spray (Spray Pyrolysis) on ordinary glass substrates. The effect of substrate temperature on the structural, morphological and optical properties of films was studied by changing it from 350°C to 425°C . The XRD patterns of the as-deposited films indicate that they are all of polycrystalline type belonging to the kesterite structure with a preferential orientation along the [112] direction. The best crystallinity was obtained for the samples prepared at 375°C . The SEM analysis show a uniformly smooth structure with condensed grains and a band gap of $E_g = 1.57\text{ eV}$ has been determined by optical measurements for the films synthesized at this temperature. If we compare these results of different elaboration temperatures, we deduce that the deposition temperature 375°C seems to be an optimum temperature

with our spray pyrolysis set up according to XRD, SEM and Raman analysis.

Acknowledgements

This work was partially funded by HORIZON project funded by AUF under contract number 59113PS019; the authors thank researchers from LMOPS (Metz, France), IES (Montpellier, France) and GOPS (Valencia, Spain) laboratories for their help during stay of LPMAER researchers.

References

- [1] H. Wang, International Journal of Photoenergy, (2011) doi:10.1155/2011/801292.
- [2] N. Kamoun, H. Bouzouita, Thin Solid Films **515**, 5949 (2007).
- [3] K. Tanaka, N. Moritake, M. Oonuki, H. Uchiki, Japanese Journal of Applied Physics, **47**, 598 (2008).
- [4] S. A. Kissin, Canadian Mineralogist, **27**, 689 (1989).
- [5] W. Shockley, H. J. Queisser, J Appl Phys, **32**, 510 (1961).
- [6] T. Friedlmeier, N. Wieser, T. Walter, H. Dittrich, H. W. Schock, Proceedings of the 14th European PVSEC and Exhibition, **10**, P4B (1997).
- [7] H. Katagiri, K. Saitoh, T. Washio, H. Shinohara, T. Kurumadani, S. Miyajima, Solar Energy Materials and Solar Cells, **65**, 141 (2001).
- [8] K.K. Jimbo, R. Kimura, T. Kamimura, S. Yamada, W. Maw, H. Araki, K. Oishi, H. Katagiri, Thin Solid Films, **515**, 5997 (2007).
- [9] T. Tanaka, D. Kawasaki, M. Nishio, Q. Guo, H. Ogawa, Phys Stat Sol (c), **3**, 2844 (2006).
- [10] K. Tanaka, N. Moritake, H. Uchiki, Solar Energy Materials and Solar Cells, **91**, 1199 (2007).
- [11] N. Nakayama, K. Ito, Appl Surf Sci, **92**, 171 (1996).
- [12] C. G. Muncea, G. K. Parkera, S. A. Holtb, G. A. Hopea, Colloids Surf A Physicochem Eng Asp, **295**, 152 (2007).
- [13] V. G. Rajeshmon, C. S. Kartha, K. P. Vijayakumar, C. Sanjeeviraja, T. Abe, Y. Kashiwaba, Solar Energy, **85**, 249 (2011).
- [14] K. Y. B. Kishore, B. G. Suresh, P. U. D. Bhaskar, R. V. Sundara, Solar Energy Materials & Solar Cells., **93**, 1230 (2009).
- [15] P. A. Fernandez, P. M. P. Salomé, A. F. D. Cunha, Thin Solid Films, **517**, 2519 (2009).
- [16] H. Park, Y. H. Hwang, B-S. Bae, J Sol-Gel Sci Technol., (2012) doi : 10.1007/s10971-012-2703-0.
- [17] P.A. Fernandes, P.M.P. Salomé, A.F. da Cunha, Semicond. Sci. Technol., **105013**, 24 (2009).
- [18] A. Ennaoui, M. Lux-Steiner, A. Weber, D. Abou-Ras, I. Kötschau, H.-W. Schock, R. Schurr, A. Hölzing, S. Jost, R. Hock, T. Voß, J. Schulze, A. Kirbs, Thin Solid Films, **517**, 2511 (2009).
- [19] K. Y. B. Kishore, P. B. Uday, G. B. Suresh, V. R. Sundara, Phys. Status Solidi A, **207**, 149 (2010).
- [20] A. C. Rastogi, S. Salkalachen, Thin Solid Films, **97**, 191(1982).

* Corresponding author: youssefarba080@gmail.com