4ème Conférence Internationale des Energies Renouvelables (CIER-2016)
Proceedings of Engineering and Technology – PET
Vol.14, pp.92 - 100

Effect of the annealing and the spraying time on the properties of CZTS thin films prepared by the "Spray sandwich" technique.

S.Mahjoubi[1,*], N. Bitri[1], H. Bouzouita[1], M. Abaab[1] and I. Ly[2].

[1]Laboratoire de Photovoltaïque et matériaux semi-conducteur (LPMS), Ecole Nationale d'Ingénieurs de Tunis (ENIT), Université Tunis El Manar, Tunis, Tunisie.

[2] Centre de Recherche Paul Pascal, Université Bordeaux 1, Bordeaux, France.

[*]E-mail: mahjoubi.sa@gmail.com

***Abstract*— We have investigated synthesis conditions and some properties of sprayed Cu_2ZnSnS_4 (CZTS) thin films in order to determine the best preparation conditions for the realization of CZTS based photovoltaic solar cells. The thin films are made by means of spraying Sandwich. In order to optimize the preparation conditions of the CZTS films, two series of experiments are performed. In the first series the sprayed duration was changed from 20min to 60min. In each series, effect annealing was investigated. The X-ray diffraction shows, on one hand, that the best crystalline was obtained after annealing for 60min as sprayed duration. On the other hand, these CZTS films exhibit the Kesterite structure with preferential orientation along the [112] direction. Raman spectrum indicated the presence of principal Stannite peak 336cm^{-1}. SEM showed that the surface of CZTS was uniform. After the annealing treatment, we estimated the optical band-gap energy of the CZTS thin film exhibiting the best crystalline as 1.5 eV which is quite close to the optimum value for a solar cell.**

***Keywords*— CZTS, thin films, Kesterite, Spray sandwich, solar cell.**

I. INTRODUCTION

Sunlight is the most abundant energy source, and the light to-electricity conversion in solar cells is one of the best developed renewable energy technologies. Ito and Nakazawa reported, over the past five years, that the quaternary chalcogenide semiconductor Cu_2ZnSnS_4 (CZTS) is one of the most promising quaternary absorber materials for thin film solar cells such as optimum band gap 1.4-1.5eV and a high optical absorption coefficient of 10^4cm^{-1} [1, 2, 3]. It is derived from CIGSe by replacing In with Zn, Ga with Sn and Se with S. Friedlmierand al.reported the conversion efficiency of 2.3%. According to Shockley-Queisser photon balanced calculations, the theoretical energy conversion efficiency of PV using CZTS absorber material is 31-33% [4].The abundant and nontoxic elements of CZTS (Cu, Zn, Sn and S) it the makes as a potential candidate for absorber layer in photovoltaic cell. CZTS has two types of crystal structures Kesterite and Stannite, only difference between them is the site position of their Cu and Zn atoms [4]. CZTS films have been deposited by physical vapor deposition methods like atom beam sputtering, thermal evaporation [5, 6], sputtering and sequential evaporation, co-evaporation [7], multistage evaporation and pulsed laser deposition [8]. Also chemical deposition methods like photo-chemical deposition, sol gel [9], and vapor phase sulfurisation of E-B evaporated precursors have been used [10].

In this present study we report CZTS thin film preparation by spray sandwich technique on glass substrates. It is a simple, versatile and low cost technique and can be used for large scale deposition of different semiconductor thin. In Spray deposition properties of the deposited film depend on several parameters of which the major ones are sprayed time, substrate temperature and spray rate. In this present study, we have investigated the influence of sprayed time; varied from 20min to 60min with the interval of 20min; and the annealing on the growth and properties of CZTS thin films.

II. EXPERIMENTAL

Frequently, Spray deposition of Cu_2ZnSnS_4 consisted of an only aqueous solution containing Thiourea $SC(NH_2)_2$, Copper chloride CuCl, Zinc chloride $ZnCl_2$, Thin chloride $SnCl_2$. In this work, we will use the sandwich spray technique in which three sprayed aqueous solutions containing respectively ZnS, SnS_2 and Cu_2S.Theses solutions were sprayed at a flow rate of 2ml/min using air and substrate temperature was fixed according to the deposition solution (**fig.1**). Cu_2ZnSnS_4 (CZTS) thin films were deposited on preheated, ultrasonically cleaned soda lime glass (SLG) and hydrochloric acid (HF).

Such that, the substrates were placed on the hot plate that is started while limiting the electric power according to the

ISSN 2356-5608

temperature at which deposition is desired (for example ZnS at 420°C). Once it has been reached we fixed the flow rate and the air flow and allowed the first solution. Once the deposition time has elapsed, we stopped spraying the first solution. We act on the adjustment of the temperature of the heating plate according to the solution which was going sprayed (**fig.1**). Once the temperature of the plate is stabilized at the new value, we sprayed the following solution. We repeat this step, until we finish all solutions needed to achieve the desired layer CZTS.

In order to determine the best condition for obtained CZTS thin films using this technique we will change the spray duration from 20min to 60min. These obtained samples are undergone with sulfur annealing under a nitrogen atmosphere during t_r=15min at a temperature of T_r=420°C. After having put 0.2 g of sulfur and as soon as the oven heats up, we triggers the flow of the nitrogen stream at a rate 1L.min^{-1} .When the temperature reaches the desired value, we decreases the flow at 0.5L.min^{-1} and we allowed to flow, even more, for t_r=15 min and T_r=420°C.

These films were investigated by studying their structural, optical and morphological properties. The crystal structural of the deposited film was identified by X-ray diffraction (XRD) and Raman spectrum. Spectral transmittance of the films was recorded in the wavelength range 300nm to 1500nm.The microstructure and the surface morphology were observed using a HITACHI TM 1000 scanning electron microscope (MEB) in research center Paul Pascal-University Bordeaux 1 (France).

III. RESULST AND DISCUSSION

A. *Structural analysis*

Fig.2 shows the XRD diffraction patterns of thin films with various sprayed times. The peaks located at 22.86° and 40.92°corresponding to the (100) and (114) orientation of CZTS (Cu_2ZnSnS_4) were appears by increased the spray duration and we observed a secondary phases peaks such as Cu_2S, ZnS and SnS_2.

Annealing is an essential stage in the formation of the material; it improves and refines the crystal structure of the layer. Since it eliminates the one hand the organic species present in the starting solution, secondly, the densification of the material. This is confirmed in this study.
Fig. 3 shows the XRD pattern of CZTS, at different spray duration (20, 40 and 60min), after annealing samples. It can be clearly seen that the XRD pattern for sulfured film at Tr=420°C, tr=15min and for 60 min spray duration match with Kesterite CZTS structure **(JCPDS00-026-0575)**. Three clear diffraction peaks were observed at 2θ(°) = 28.53°; 29.67° and 32.99° corresponding to (112), (103) and (200) planes for Kesterite CZTS. XRD analysis detected the presence of ZnS and SnS secondary phases, their intensity decrease with increase the spray duration. XRD analysis confirmed the presence of their binary compounds; this fact reveals the importance of Raman analysis distinguishes between their binary compounds and CZTS. Form the XRD pattern; it can be observed the presence of CZTS with a preferential orientation of (112) only after annealing for 60min spray duration.

The crystallite size is esteemed from the (112) peak using the Debey – Scherrer's formula:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad [11]$$

Where λ is the wavelength of Cu-K_α radiation (1.541874Å),Θ is the diffraction angle, K=0.9 and β is full-width at half maximum (FWHM).The microstrain (ε) developed in these thin films was calculated with the following relation

$$\varepsilon = \frac{\beta \cos \theta}{4} [12]$$

The lattice parameter (a, b and c) of tetragonal Cu_2ZnSnS_4 type structure can be calculated by the following formula:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2 (\frac{a^2}{c^2})}}$$

Where d_{hkl} is the inter-planar spacing corresponding to Miller indices h, k and l.
The crystallite size, microstrain and lattice parameter (a, b and c) are found to be 49.43nm, 7×10^{-4} and (a=b=5.5 and c=10.81) respectively.
Sulfured films were further analyzed by Raman spectroscopy to identify the possible secondary phases in the deposited films and would allow a more detailed discussion regarding the origin of the XRD peaks. Raman bands of CZTS are reported at 233, 260, 292, 336, 350, 363 and 377cm^{-1} (**fig.4**).The existence of CZTS thin film is confirmed by the most intense peak at 336cm^{-1} and the shoulder peaks at 350and 363cm^{-1}. The reported Raman bands of tetragonal Cu_2SnS_3 are at 303cm^{-1}, for SnS are at 222 and 358cm^{-1} and for SnS_2 are at 312cm^{-1}. Theses peaks could be attributed to the presence of secondary phases in the CZTS thin films performed at 60min under sulphur annealing. These studies both XRD and Raman confirm the formation of CZTS thin film [13, 14]. These results show that the CZTS thin films were performed only at 60 min and after thermal annealing (t_r=15min and T_r=420°C) with Kesterite structure [15].

B. *Morphological properties*

Fig. 5 and **6**; shows the SEM images of films deposited at 60min before and after annealing. The CZTS obtained after annealing micrographs show that the films uniformly cover the substrate. The surface morphologies of thin films before annealing (**fig.5**) show a non-uniform distribution of particles that are densely packed on the surface of the films. This can be attributed to the presence of ZnS and Cu_2SnS_3secondary phases.
With annealing, an increase in the average grain size is observed. Increase in grain size improves the performance of a polycrystalline CZTS thin film with decrease in grain

ISSN 2356-5608

boundaries that increases the effective diffusion length of minority carriers [16].**Chalapathi et al**. [17] observed improved grain size after annealing the thermally evaporated CZTS films at 580°C in sulfur atmosphere. They have observed larger crater like area and a few voids on the surface, which they concluded may be due to insufficient sulfur vapor pressure. Voids on the absorber layer in the thin film solar cells lead to low conversion efficiency because the generated carriers are disturbed at both grids [18]. In this work, compact uniform morphology without voids is observed due to excess amount of sulfur incorporated during the annealing. Thickness of the films after and before is calculated by the cross- section of SEM images and found to be: 1.18µm and 970nm, respectively

C. Optical properties

1) Transmission and reflection spectra: The transmission spectrum (fig.7) shows the appearance of a peak at $\lambda = 693$ nm. This transparency seen in the interval $693 \pm \Delta\lambda$, avec $\Delta\lambda = 165$nm, gives us the impression that our material behaves like an optical filter with a transmission that does not exceed 12% in the same wavelength range. Furthermore this low transmission over a range of 200 nm to 1200 nm allows giving to the thin layer of CZTS the character to be a good absorber of light.

2) Gap energy: In order to calculate the optical band gap energy (E_g) of these thin films, the absorption coefficient can be estimated as:

$$\alpha = \frac{1}{d}\ln(\frac{(1-R)^2}{T}) \quad [20]$$

The energy gap of CZTS thin layer CZTS has been estimated from the graph $(\alpha h\nu)^2$. The extrapolation of straight line portions to zero absorption coefficient ($\alpha = 0$) leads to the estimation of band gap energy value. In the case of a direct transition, the optical band gap energy E_g is giving by the following relation.

$$\alpha h\nu = (A(h\nu - E_g))^{1/2} \quad [21]$$

Fig (8 and 9) shows the band gap plots of CZTS thin films with different spray times (20, 40 and 60min) after and before annealing. From the graph it was observed that the band gap of the CZTS thin films before annealing varied from 1.96 to 2.33eV and after annealing varied from 1.49 to 1.74eV.

The direct optical band gap of Cu_xS reported earlier in the literature is found to vary from1.7eV to 2.16eV based on the value of x [22]. The presence of secondary phases having higher band gap may show an increase in the measured optical band gap of the materials. The sample with 40min after annealing has band gap 1.74 eV which corresponds to the Cu_xS. The change in the optical band gap of this sample is due to compositional difference.

It is clear that the thin film of CZTS developed at 60 of spraying minutes before or after annealing has the high absorption coefficient α. The absorption coefficient near the fundamental absorption edge is ~10^5 cm^{-1}. This shows that we can use this as an absorber layer for solar cell.At the absorption edge, the refractive index "n" and the extinction coefficient "K" were calculated from these following relations [23]

$$n = \frac{(1+R)+\sqrt{4\times R-(1-R^2)\times R^2}}{1-R}$$

$$K = \frac{\alpha\lambda}{4\Pi}$$

Where R is the experimental values of Reflection, λ is the wavelength for Cu radiation and α is the absorption coefficient.**Fig.10** shows the refractive index (n) and the extinction coefficient (K) for CZTS thin film obtained after annealing and for 60min spray duration. The refractive index decreases with increasing wavelength from 1.68 (at ʎ=500nm) to 1.55 (at ʎ= 900nm). And it is clear that the extinction coefficient is negligible; it is less than 5.10^{-3} at 900 nm.

Using the model of Wemple–DiDomenico and Spitzer- Fan we can describe the dispersion of the refractive index n(λ) and determinate a different dielectric constants.

Fig.12 show the plot of $(n^2-1)^{-1}$ versus $(h\nu)^2$ $(eV)^2$, its can be illustrate for the determination of the single oscillator energy E_0 and the strength of inter band optical transition of dispersion energy E_d. Using this following relationship:

$$n^2(h\nu) = 1 + \frac{E_0 E_d}{E_0^2 + (h\nu)^2} \quad [24]$$

The values of E_0 and E_d for CZST thin films obtained after annealing deposited at 60 min spray duration is respectively 1.97eV and 1.54eV.

The Urbach energy provides information on band energy changes and disorder structural thin films **(fig.11).**
After this study; we can say that the sandwich technique is effective to develop thin film CZTS well suited for solar cell applications.

ISSN 2356-5608

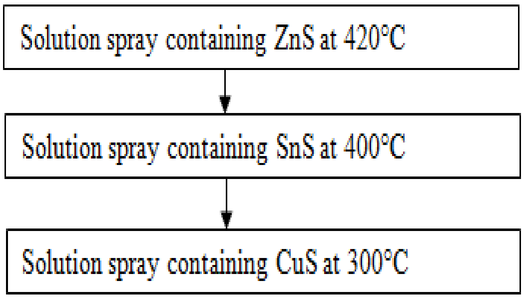


Fig.1: *Flow chart of temperature process*

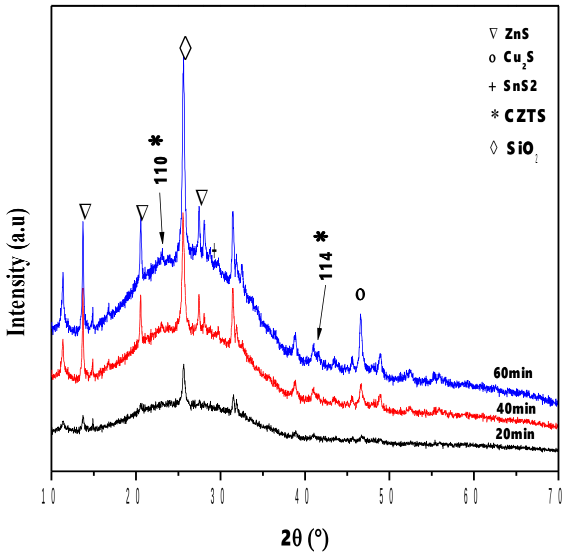


Fig. 2: *X-ray diffraction patterns for thin films prepared at different spraying times (20min, 40min and 60min)*

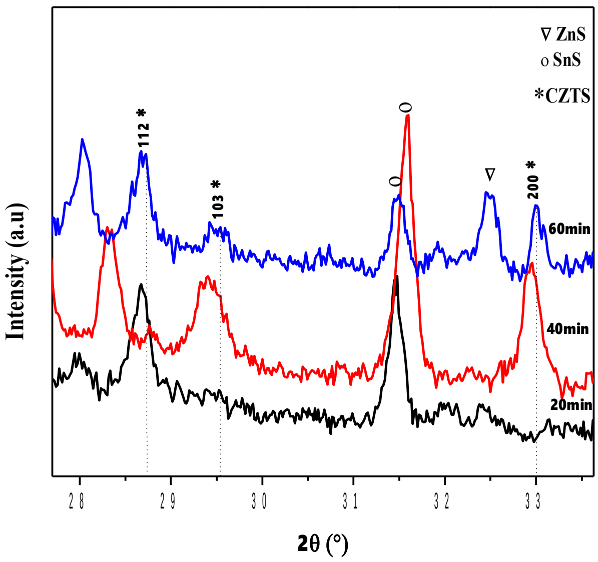


Fig.3: *X-ray spectra of samples CZTS deposited for different spray duration [20min, 40min and 60min] and after annealing for Tr=400°C and* t_r *=15min*

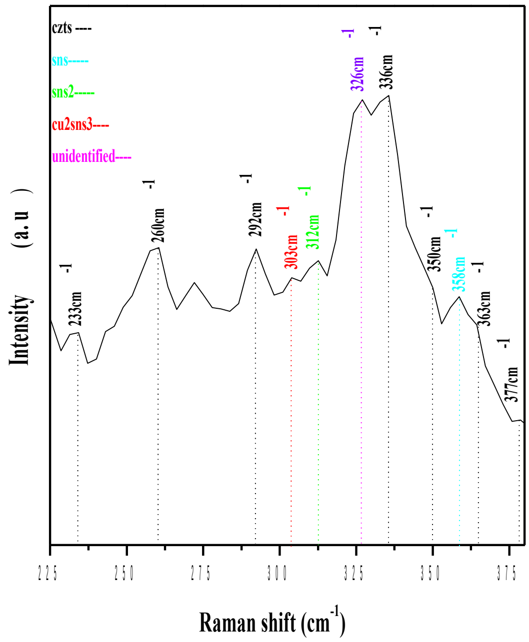


Fig. 4: Raman spectrum of CZTS films prepared at 60min spray duration and after annealing *for Tr =400°C and* t_r *=15min*

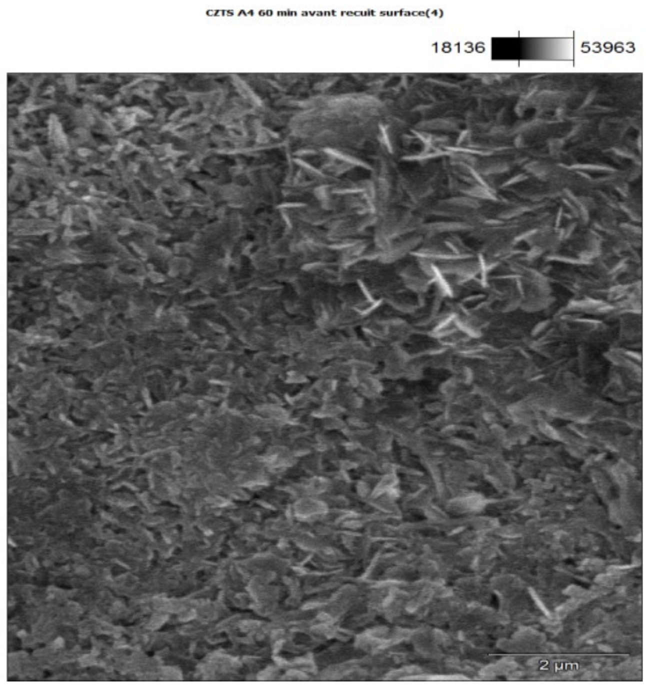


Fig. 5: SEM micrograph of CZTS samples deposited at 60min duration spray before annealing

ISSN 2356-5608

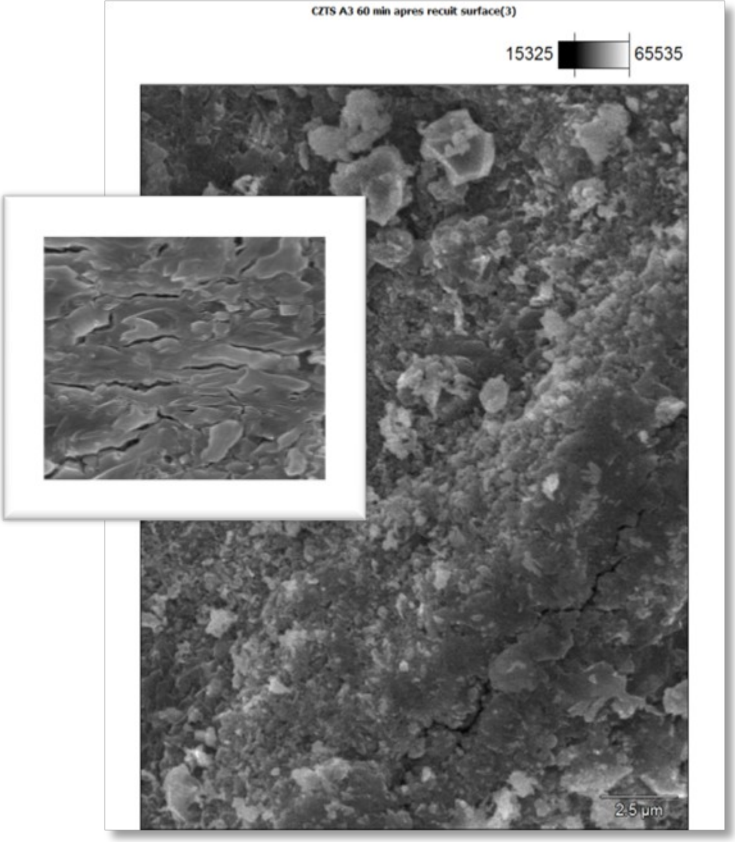


Fig. 6: SEM micrograph of CZTS samples deposited at 60min after annealing *for Tr=400°C and t_r=15min*

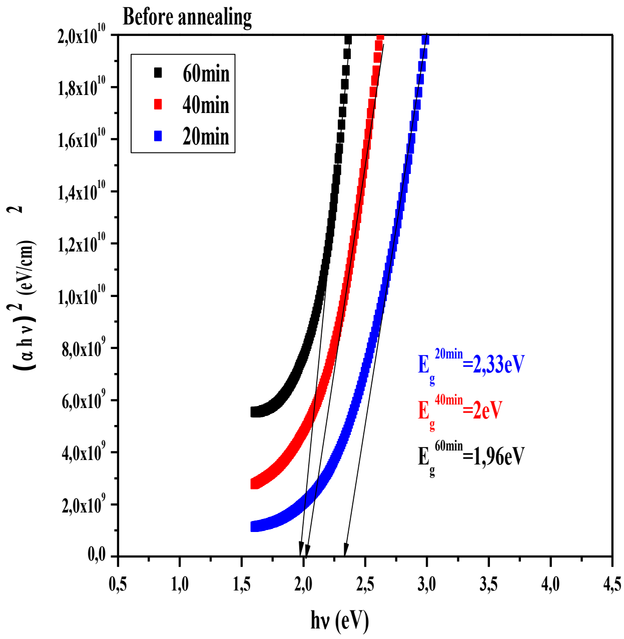


Fig. 8: Determination of the gap energy of thin films before (annealing for different duration spraying (20, 40 and 60 min

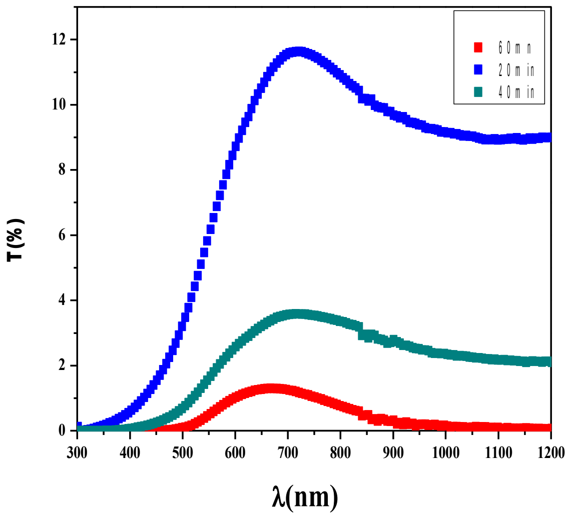
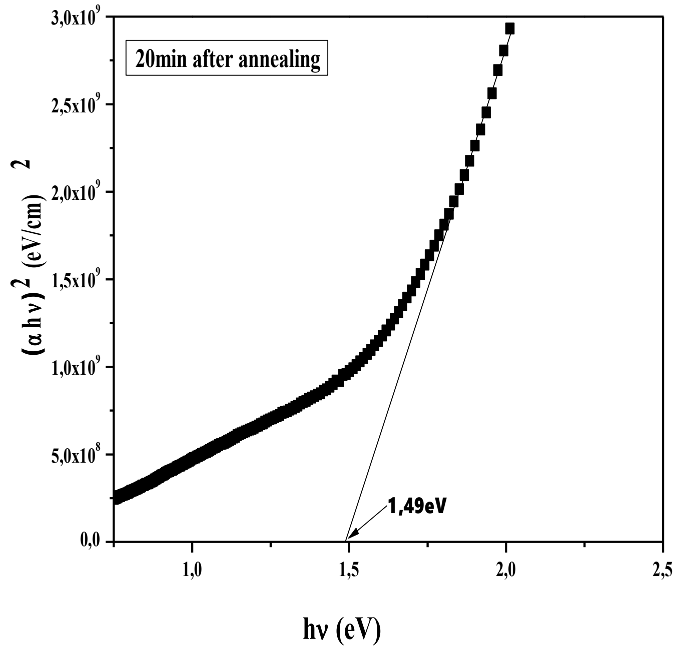


Fig. 7:Transmission (%T) spectra of CZTS films *deposited for different spray duration [20min, 40min and 60min] and after annealing for Tr=400°C and t_r=15min*

ISSN 2356-5608

4ème Conférence Internationale des Energies Renouvelables (CIER-2016)
Proceedings of Engineering and Technology – PET
Vol.14, pp.92 - 100



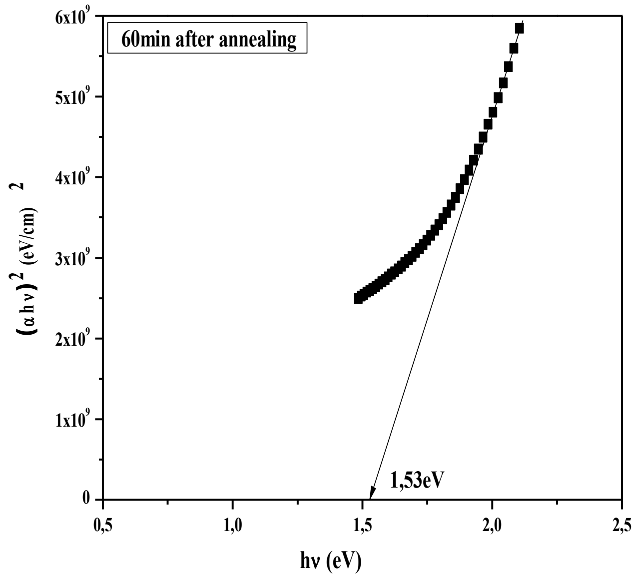
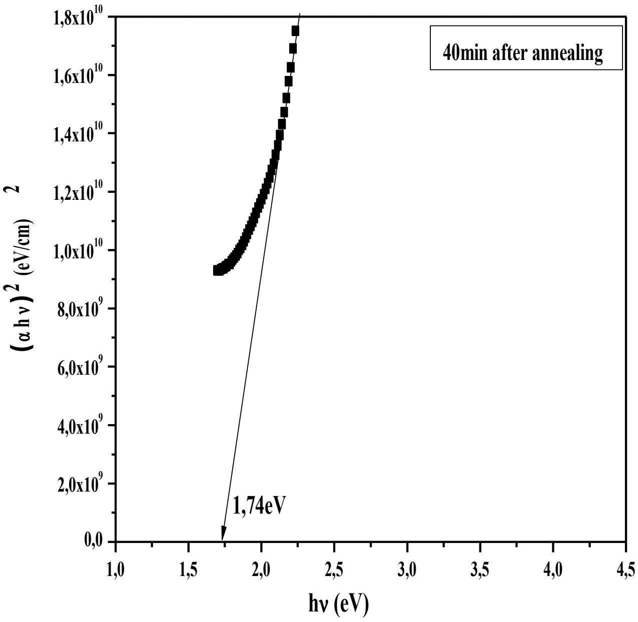
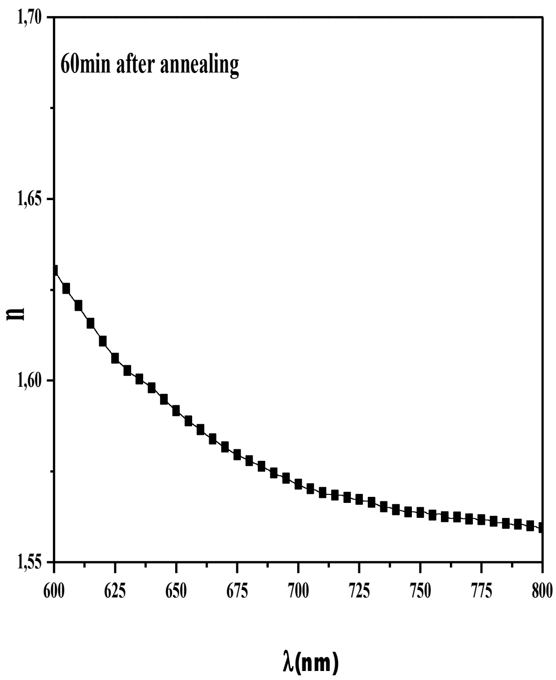


Fig. 9: Determination of the gap energy of thin films after annealing for different duration spraying (20, 40 and 60 min) *(Tr=400°C and* t_r*=15min)*





ISSN 2356-5608

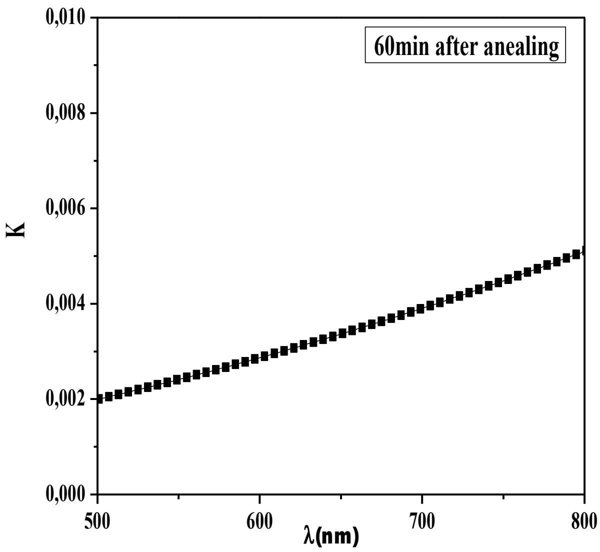


Fig.10: Refraction index and the extinction coefficient of CZTS deposited of 60min spray duration and after annealing (Tr=420°C and tr=15min)

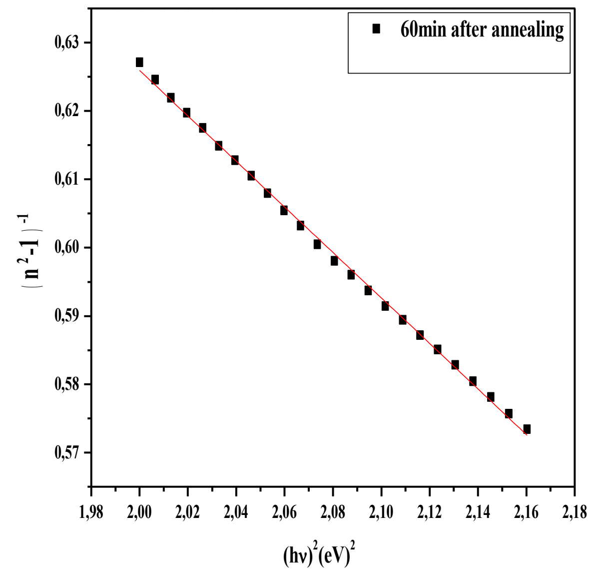


Fig. 12: Plot of (n2-1)$^{-1}$ versus (hν)^2 of CZTS thin films after annealing deposited at 60min for duration spray

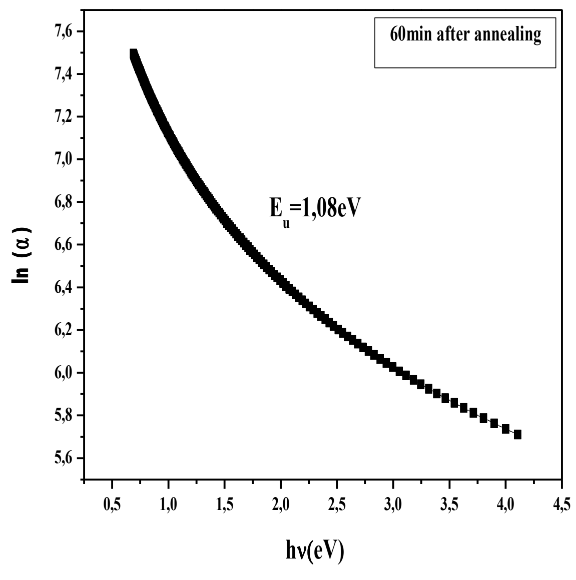


Fig.11: Determination of the Urbach energy for CZTS thin films deposited for 60min spray duration and after annealing

IV. CONCLUSION

Cu_2ZnSnS_4 thin films have been successfully fabricated using the sandwich technique by spray. The results showed that the polycrystalline structure of good quality was formed after annealing with a time of spraying 60min. The p-type CZTS film with an absorption coefficient of 10^5 cm^{-1} obtained by this new process. The optical energy band gap of the CZTS sample is about 1.55 eV, which is very close to the optimum value for a solar cell. These results show that the CZTS films can be used as an absorber in the solar cells.

REFERENCES

[1] H. Katagiri, K. Jimbo, K. Moriya; Solar cell without environmental pollution by using CZTS thin film; Proc. 3rd World Conf. on Photovoltaic Solar Energy Conversion, Osaka, Japan; (2003).

[2] Xianzhong Lin, JaisonKavalakkatt, Kai Kornhuber, Daniel Abou-Ras, Susan Schorr, Martha Ch. Lux – Steiner and Ahmed Ennaoui; Synthesis of $Cu_2Zn_xSn_ySe_{1+x+2y}$ nanocrystals with wurtzite derived structure; RSC Advances, (2012).

[3] H. Katagiri, N. Ishigaki, T. Ishida; Characterization of Cu_2ZnSnS_4 thin films prepared by vapour phase sulfurization; Jpn. J. Appl. Phys, (2001).

[4] S.M.Bhosale,M.P.Suryawanshi,J.H.Kim, A.V.Moholkar; influence of copper concentration on sprayed CZTS thin films deposited at high temperature; ceramics international ; 41(2015)8299-8304.

[5] Th. M. Friedlmeier, N. Wieser, Th. Walter, H. Dittrich, H. W. Schock; Proc. of 14th European Photovoltaic Solar Energy Conf. and Exhibition, Barcelona, Spain; P4B; (1997).

ISSN 2356-5608

[6] K. Tanaka, N. Moritake, H. Uchiki; Preparation of Cu_2ZnSnS_4 thin films by sulfurization sol-gel deposited precursors; Sol. Energy Mater. Sol. Cells (2007).
[7] A. Redinger and S. Siebentritt; Co evaporation of $Cu_2ZnSnSe_4$ thin films; Appl. Phys. Lett, (2010).

[8] L. Sun, J. He, H. Kong. F. Yue. P. Yang. and J. Chu. Sol; Thin film solar cells from abundant materials; Energy Mater. Sol. Cells; (2011).
[9] K. Tanaka, Y. Fukui, N. Moritake and H.Uchiki; Chemical composition dependence of morphological and optical properties of Cu_2ZnSnS_4 thin film solar cell efficiency; Sol Energy Mater.Sol.Cells, (2011).
[10] N. Nakayama, K. Ito; Sprayed films of stannite Cu_2ZnSnS_4; Appl. Surf. Sci (1996).
[11] E. Valkonen, C.G. Ribbing and J. E. Sundgren, Optical constants of thin Silver and Titanium Nitride Films, Proc. SPIE, 652, 235-242.
[12] J.Henry, K.Mohnaraj, G. Sivakumar; Electrical and optical properties of CZTS thin films prepared by SILAR method; Journal of Asian Ceramic Societies(2016) 81-84.
[13] S. M. Bhoale, M. P. Suryawanshi, M. A. Gaikwad, J. H. Kim, A.V. Moholkar; Influence of Growth temperatures on the properties of photoactive CZTS thin films using a spray pyrolysis technique; Materiels letters (2014).
[14] V. G. Rajeshmon, M. R. Rajesh Menon, C. SudhaKartha, K. P. Vijayakumar; Effect of copper concentration and spray rate on the properties Cu_2ZnSnS_4 thin films deposited using spray pyrolysis; Journal of Analytical and Applied Pyrolysis (2014)

[15] Pay–Yu. Lee, Sheng-Po. Chang and Shoou-Jinn Chang; Fabrication and photo electrochemical behavior of n-type $Cu_2ZnSnSe_4$ thin film Electrodes prepared via non vacuum Nanoinks process; ESC Journal of solid state Science and technology, (2013).

[16] H. Park, Y. H. Hwang, B. S. Bae; Sol–gel processed Cu_2ZnSnS_4 thin films for a photovoltaic absorber layer without sulfurization; J. Sol-Gel Sci. Technol. (2013).

[17] U. Chalapathi, S. Uthanna,V. Sundara Raja, Growth of Cu2ZnSnS4 thin films by a two stage process—Effect of incorporation of sulfurat the precursor stage; Sol. Energy Mater. Sol. Cells (2015).

[18] S. W. Shin, S. M. Pawar, C. Y. Park, J. H.Yun, J. H. Moon, J. H. Kim, J. Y. Lee; Studies on Cu_2ZnSnS_4 (CZTS) absorber layer using different stacking orders in precursor thin films; Sol. Energy Mater. Sol. Cells (2010).

[19] Sawanta S.Mali, Bharmana M. Patil; Novel synthesis of Kesterite Cu_2ZnSnS_4nanoflakes by successive ionic layer adsorption and reaction technique: Characterization and application; ElectrochimicaActa (2012).

[20] R.Touati, M.BenRabeh, M.Kanzari; Effect of post-sulfurization on the structural and optical properties of Cu2ZnSnS4 thin films deposited by Vacuum evaporation method; Thin solid Films 582(2015)198-202.
[21] S.M.Bhosale, M.P.Suryawanshi, J.H.Kim, A.V.Moholkar; Influence of copper concentration on sprayed CZTS thin films deposited at high temperature; Ceramics Internatinoal 41(2015)8299-8304.
[22] Y. B. Kishore Kumar, G. Suresh. Babu, P. UdayBhaskar and V. Sundara Raja; Preparation and characterization of spray-deposited Cu_2ZnSnS_4 thin films; Solar Energy Materials and solar cells (2009).
[23] M. Ben Rabeh, M. Kanzari; Thin solid films 519 (2011) 7288-7291.
[24] H.Yoo, J.Kim, "Comparative study of Cu2ZnSnS4," Solar Energy Materials and Solar Cells, vol.95, pp.239-244, 2011.

ISSN 2356-5608