The influence of the deposition condition on crystal growth and on the band gap of $CuSbS_2$ thin film absorber used for Solid State Solar Cells (SSSC)

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The paper discus the influence of the precursors weight ratio on the value of the $CuSbS_2$ thin film band gap, used as absorber for solid state solar cells. The depositions were made by Spray Pyrolysis Deposition (SPD) using $CuCl_2{\cdot}2H_2O$, $(CH_3COO)_3Sb$, and H_2NCSNH_2 as precursors in 1: 2.57: 5. 71 - 1:6.86:5.71 weight ratio. The obtained films were analyzed via X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) current-voltage measurement recorded in dark and UV-VIS Spectroscopy. It is observed that the precursors weight ratio of the films, influences not only the crystal growth but also the value of the $CuSbS_2$ band gap.

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1. Introduction

The solid state solar cells (SSSC) are an alternative to the dye sensitized solar cells in the trend firstly stated by Graetzel, (1991) [1], having all the compounds made from inorganic and solid materials. The SSSC is formed when an n-type nanoporous wide band gap semiconductor is infiltrated with a p-type semiconductor on a nanometer scale. The most efficient cell, (4%, [2]), has the structure: TCO (transparent conducting oxide)/ dense TiO_2 anatase/ nanoporous TiO_2 anatase (n-type transparent semiconductor)/ $CuInS_2$ absorber (p-type semiconductor)/ Au.

The main topic in the cell research is to find new inorganic semiconducting materials as optical absorbers.

The requirements for the ideal absorber solar cell material are:
- band gaps in range of 1.0 and 1.6 eV for efficiency above 30% (AM1.5), or in the range of 0.7 to 2.0 eV for efficiency over 20%.
- a high light absorption coefficient of the materials,
- direct band structure,
- the availability of the semiconductor material in the n and p-type varieties,
- non-toxic materials,
- good photovoltaic conversion efficiency,
- readily available,
- easy, reproducible deposition technique, suitable for large area production,
- long-term stability, chemical stability and, most important,
- the formation of a photo-active interface with the semiconducting oxide, [3, 4, 5].

The absorber $CuInS_2$ (CIS) is part of the I-III-VI_2 group of semiconductors, with chalcopyrite structure. It is suitable for photovoltaic applications, because it is stable, non-toxic, has a high absorption coefficient (more than $10^4 cm^{-1}$) with a direct band of 1.5.eV.

An alternative to replace the $CuInS_2$ is $CuSbS_2$; it is part of the same I-III-VI_2 group of semiconductor with chalcopyrite structure and the ionic radius of indium and antimony are almost equal. $CuSbS_2$ is a direct semiconductor, with the band gap 1.52 eV, and its properties match with the requirement for the photovoltaic materials, [6, 7]. Another reason is the price of antimony which is lower than for indium.

The proposed structure of the 3D cell is TCO/ dense TiO_2 anatase/ nanoporous TiO_2 anatase/ $CuSbS_2$ (absorber)/ Au, Fig. 1.

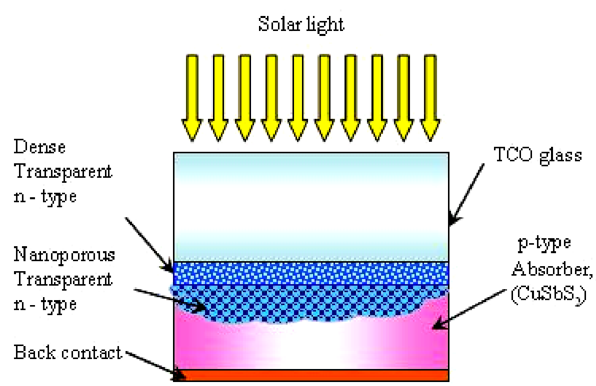


Fig. 1. The structure of a 3D solar cell.

So far, the literature mentions the deposition of $CuSbS_2$ thin films only through annealing chemically deposited Sb_2S_3–CuS thin films, [6].

Our work propose for deposition of $CuSbS_2$ thin films Spray Pyrolysis Deposition (SPD) technique, a relative simple and low cost deposition method, which is suitable for large area thin films deposition.

The paper discus the influence of the deposition condition (precursor weight ratio) on the crystal growth and also on the value of the $CuSbS_2$ thin film band gap used as absorber for SSSC.

The band gap is an important parameter in the development of the new material and its use as p-type absorber semiconductor in photovoltaic applications, in our case solid state solar cells.

2. Experimental

The $CuSbS_2$ films are deposited on the TCO (transparent conducting oxide, F doped SnO_2 coated glass) at different precursor weight ratio as presented in Table 1. The TCO glass (F doped SnO_2 coated glass, Libbey Owens Ford – TEC 20/2.5mm), is cleaned by successive immersion in ethanol and acetone in an ultrasonic bath and dried in a nitrogen flow.

Table 1. The parameters varied in the deposition of $CuSbS_2$ layers by SPD.

Tests	Substrate	$CuCl_2 \cdot 2H_2O$: $(CH_3COO)_3Sb$ H_2NCSNH_2	T (°C)
(A)	TCO	*1: 2.57: 5.71*	240
(B)		*1: 4.29: 5.71*	
(C)		*1: 6: 5.71*	

For obtaining *$CuSbS_2$ absorber thin films,* copper (II) chloride dehydrate, $CuCl_2 \cdot 2H_2O$, antimony (III) acetate, $(CH_3COO)_3Sb$, 99.99%, and thiourea H_2NCSNH_2, 99%, (both as sulphur source and as complexation agent) are used as precursors in 1: 2.57: 5. 71 - 1:6.86:5.71 weight ratios range. Few drops of HCl conc. are added to increase the solubility of antimony acetate.

During spraying, a pressure of carrier gas at 1.2 bars (Ar), and a 27 cm of distance between the spraying nozzle and the heater are fixed.

The obtained films were analyzed using X-Ray Diffraction (XRD, Bruker D8 Advance Diffractometer), Scanning Electron Microscopy (SEM, Jeol JSM-5800LV), current-voltage (I-V) measurement recorded in dark (DC Source Meter, Keithley, model 2400) and UV-VIS Spectroscopy **(**UV-VIS spectrophotometer Perkin Elmer Lambda 25 UV/VIS).

3. Results and discussion

Previous studies showed that after deposition parameters (temperature, precursor weight ratio) were varied and optimized, $CuSbS_2$ thin films with good diode behaviour were obtained at Sb-rich films and not as Cu-rich films as initially expected, [8]. Literature mentions the obtaining of good diode behaviour for the chalcopyrite films (e.g. $CuInS_2$) at small Cu-rich films.

The XRD patterns Fig. 2, of the $CuSbS_2$ films deposited of different precursor weight ratio identified the formation of orthorhombic $CuSbS_2$ film according to JCPDS: 24-0347, with the representative peaks at 2θ = 28.713, 47.331, and 56.439, corresponding to the (040), (160), and (002) directions.

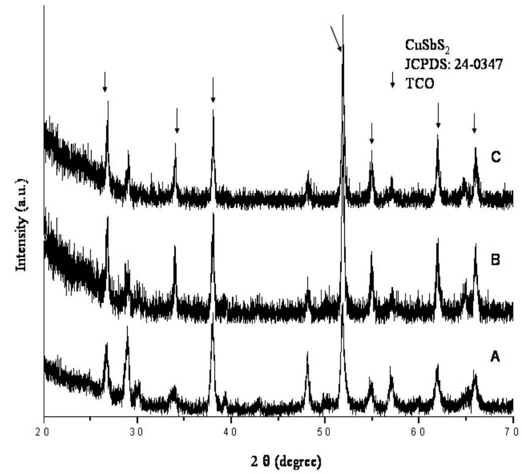


Fig. 2. XRD of $CuSbS_2$ thin films deposited on TCO substrate at different precursors concentration, [9].

The crystallites grain size for the three samples were calculated using the Scherrer formula, for the (0 4 0) peak, (2θ = 28.713).

$$D = \frac{0.9\lambda}{\beta \cos\theta}, \quad (1)$$

Where:

λ – the wavelength (0.179021 nm),

β - the full-width at half-maximum of the peak, in radian and

θ - the Bragg angle.

The calculated values for the three samples are presented in Table 2 and prove that the values of crystallites grain size increase with increasing of the Sb amount.

Table 2. D values of the $CuSbS_2$ films deposited at different precursor weight ratios.

Sample	2θ (degree)	Orientation	D (nm)
A	28.713	(040)	49.68
B			62.89
C			83.58

The SEM pictures of $CuSbS_2$ films deposited at different precursor weight ratio proved that by increasing the antimony amount, the films are transforming from grain aggregates with a fibber texture (A sample) in films with porous morphology (C sample), Fig. 3.

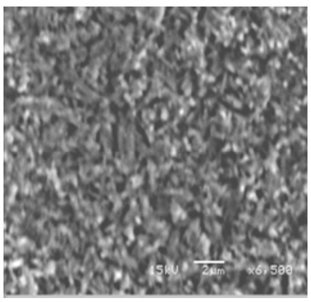
Comparing the crystallites grain size calculated from XRD with the values from SEM is observed that aggregates of crystallites are formed. The values of grains / aggregates ($\frac{D}{Agg}$) are presented in Table 3.

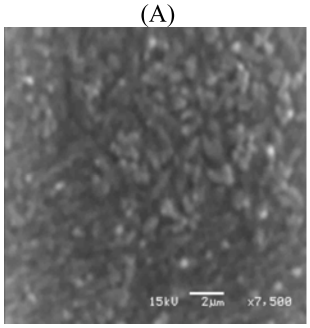
Table 3. D values of the $CuSbS_2$ films deposited at different precursor weight ratios.

Sample	D (nm)	Agg (nm)	$\frac{D}{Agg}$
A	49.68	400	8.05
B	62.89	450	7.15
C	83.58	500	5.98

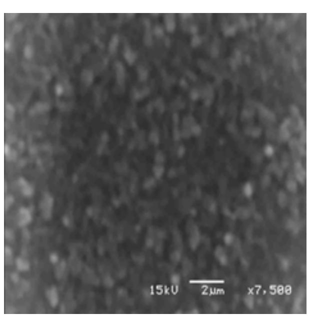
The electrical measurements (current-voltage curves) of the films are registered in dark conditions, Fig. 4.

The current-voltage (I-V) curves prove the formation of $CuSbS_2$ thin films with diode behavior that can be improved by increasing the amount of antimony in the films.


(A)



(B)



(C)

Fig. 3. SEM pictures at different precursor concentration ratio

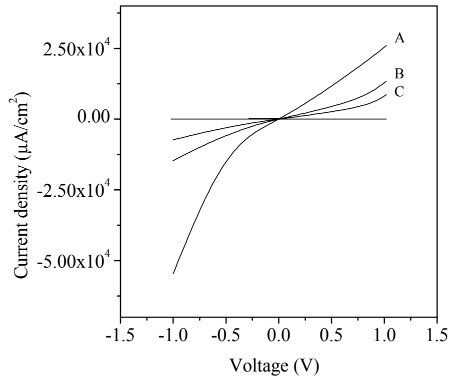


Fig. 4. I-V dark curves of $CuSbS_2$ film deposited at different precursor weight.

In order to determine the absorption coefficient and the band gap values, Eg, for the three samples the optical transmittance spectra is used. The absorption coefficient was calculated using the relation:

$$\alpha = \ln \frac{(1/T)}{t}, \quad (1)$$

Where:

T - the transmittance and

t - the thickness of the film.

The thickness of the film was evaluated from de UV spectrum and the average value corresponds to 1.650 nm $CuSbS_2$ thin film. The band gaps energy was obtained by plotting the optical absorption, $(\alpha hv)^2$ vs. the photon energy, (hv), and extrapolating the linear portion of the curve to $(\alpha hv)^2 = 0$, Fig. 5.

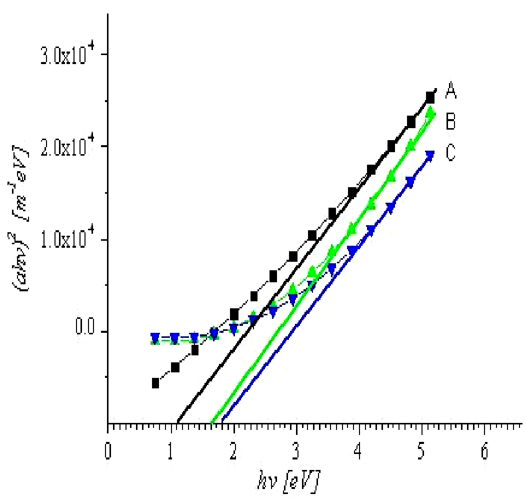


Fig. 5. Band gap energy of $CuSbS_2$ deposited at different precursor weight ratio.

The obtained Eg for the three samples are presented in Table 3 and it is observed that Eg increase with increasing of the Sb amount, and with the grain crystallite size in the films.

Table 3. E_g values of the $CuSbS_2$ films.

Sample	A	B	C
Eg (eV)	1.1	1.7	1.8

The values are close to the literature prediction, 1.5 eV. The difference in the values can be related to the different morphologies, with particular emphasis on the grain size and not on the aggregates. This can be well explained due to the porous, open structures.

The I-V curves show the best photovoltaic response to the sample with the highest band gap. This can be explained, considering that photovoltaic performance depends on the E_g but mostly on the Fermi level position. Thus, larger E_g match with the required condition.

4. Conclusions

The paper investigates the influence of the precursor weight ratio on crystal growth in the films and also on the band gap value.

The films were deposited using $CuCl_2 \cdot 2H_2O$, $(CH_3COO)_3Sb$, 99.99%, and H_2NCSNH_2, 99%, as precursors in 1: 2.57: 5. 71 - 1:6.86:5.71 weight ratios range and at 240°C.

The XRD patent proved the formation of orthorhombic $CuSbS_2$ thin film according to JCPDS: 24-0347 and with crystallite size increasing with increasing of antimony amount in the films. Comparing the crystallites grain size calculated from XRD with the values from SEM is observed that aggregates of crystallites are formed.

The values of E_g are influenced by the deposition parameter (precursor weight ratio) and by the crystallite size. With increasing of antimony amount and the crystallite size the Eg increase also.

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