KESTERITE THIN FILMS OF Cu_2ZnSnS_4 OBTAINED BY SPRAY PYROLYSIS

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ABSTRACT: Thin films of Cu_2ZnSnS_4 (CZTS) were deposited using the spray pyrolysis method as relatively fast and vacuum-free method. Obtained samples were analyzed using the X-Ray Fluorescence, grazing incidence X-Ray Diffraction and Raman Spectroscopy techniques. Analysis showed close to stoichiometry composition of the films with kesterite type structure but poor crystalline quality and possible existence of secondary phases. To improve the quality of the films, the as-prepared layers were annealed in the presence of elemental Sn and S. Comparison of the results before and after annealing showed a strong improvement of the crystalline quality and a significant reduction of concentration of secondary phases of the films without significant change of composition. The measured optical band gap is equal to 1.52 and 1.55 eV in the as-prepared and annealed films, respectively. The optical absorption coefficient is found to be > 10^4 cm^{-1}.

Keywords: Kesterite, Thin Films, Spray Pyrolysis, XRF, Raman

1 INTRODUCTION

I-III-VI_2 type compounds as well as CdTe are promising materials for high-efficiency thin film solar cells. The efficiency of $CuIn_{1-x}Ga_xSe_2$ based solar cells is reported to reach 20.3 % [1]. However, for a large-scale production the supply of In, Ga and Se could pose a problem due to the low abundance of these elements in the earth's crust (Cd: 3×10^{-5}%, Ga: 10^{-3}%, In: 10^{-5}%, Se: 8×10^{-5}%, Te: 10^{-6}%).

Cu_2ZnSnS_4 (CZTS) is a promising material for absorber layers of thin film solar cells, since CZTS thin films have the suitable optical band-gap energy of 1.4 – 1.5 eV and a large optical absorption coefficient of 10^4 cm^{-1}. In addition, all the constituents of CZTS thin films are abundant in the crust of the earth and non-toxic [2].

In the recent years the efficiency of the solar cells based on $Cu_2ZnSn(S,Se)_4$ (CZTSSe) absorber layers have shown encouraging growth from 2.6 % in 2001 [3] to 10.1 % in 2012 [4]. The latter was observed in CZTSSe solar cells using a hydrazine-based hybrid slurry approach. However, hydrazine is a highly toxic and very unstable compound that requires extreme caution during handling and storage.

It is highly desirable to develop a robust, easily scalable and relatively safe solution-based process for the fabrication of a high quality CZTS absorber layer. Spray pyrolysis is one of the methods which are non toxic, cheap, fast and vacuum-free [5-7].

In this work we report the preparation of CZTS thin films deposited on glass substrates by using spray pyrolysis method. Compositional, structural, optical, and electrical properties of the as-deposited and annealed CZTS thin films have been studied. The investigated Cu_2ZnSnS_4 layers show a p-type conductivity and an optical absorption coefficient and a band gap suitable for thin film solar cells.

2 EXPERIMENTAL DETAILS

Thin films of Cu_2ZnSnS_4 were deposited using the spray pyrolysis method from aqueous and hydro-alcoholic solutions with molar concentrations of pure chemical compounds equal to:

- 0.08 M of $CuCl_2$ with $2H_2O$;
- 0.04 M of $SnCl_4$ with $5H_2O$;
- 0.04 M of $Zn(O_2CCH_3)_2$ with $2H_2O$;
- 0.32 M of $SC(NH_2)_2$.

In the 100 ml of solution of the components listed above 3 ml of C_2H_5OH were added to improve its stability. The described solution was deposited onto glass substrates at a temperature of ~ 450 °C using a specially designed setup shown in Figure 1. It contains four main units:

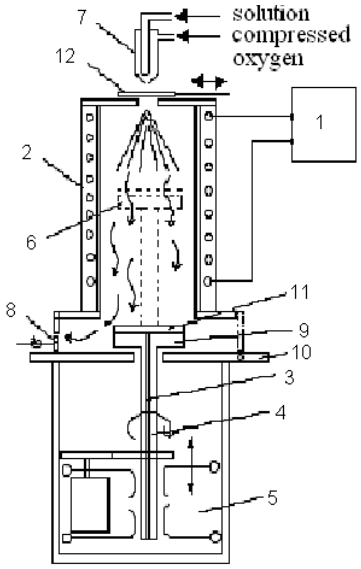

Figure 1: Schematic of the developed setup for the deposition of CZTS thin films: 1-power unit; 2-electric furnace; 3-thermocouple; 4-rotating stage; 5-mechanism for stage rotation and displacement; 6-stage position during the layer preparation; 7-system of spraying; 8-system of exhaust ventilation; 9-stage position during loading of the glass substrate; 10-screen; 11- glass substrate; 12-shielding plate.

(i) the pulverization system, (ii) the system for displacement and rotation of the deposition stage where the substrate is placed, (iii) the system of substrate temperature control and (iv) the system for evacuation of residual products of the pyrolysis. The system which ensures the substrate temperature control consists of an electric furnace and a device for automatic adjustment of the deposition temperature. The glass substrate is placed on the deposition stage which is moved by means of a displacement mechanism in the deposition zone of the electric furnace. The latter mechanism provides the rotation of the stage at a constant speed of 60 rotations per minute. This is required to obtain CZTS thin films with a uniform thickness on the entire surface of the glass substrate.

The aqueous and hydro-alcoholic solutions mentioned above were sprayed with compressed oxygen into the furnace where the glass substrate is placed. The CZTS thin film was then formed as a result of thermal decomposition of the solution as follows:

$2CuCl_2 \cdot 2H_2O + Zn(O_2CCH_3)_2 \cdot 2H2O + SnCl_4 \cdot 5H2O + 4SC(NH_2)_2 \rightarrow Cu_2ZnSnS_4(s) +$gaseous products

The film thickness was varied between 1 and 3 μm by adjusting the deposition time.

To improve the crystalline quality of the film grains, the thin films were annealed in an evacuated volume at 450 °C for 30 min. In order to prevent from loss of S and Sn, the annealing was performed in the presence of elemental sulphur (10 mg/cm^3) and tin (5 mg/cm^3).

The samples were characterized using the X-Ray Fluorescence (XRF), grazing incidence X-Ray Diffraction (GIXRD), Raman Spectroscopy (RS) techniques as well as optical transmission and electrical transport measurements. The XRF measurements were performed on a Fischerscope X-ray XDV-SDD with a micro-focus X-ray tube equipped with a wolfram anode and a beryllium window (50 kV), and a silicon drift detector. The GIXRD data were collected using a PANalytical X'pertPro MPD diffractometer equipped with CuKα radiation (λ=1.54056 Å). Raman spectra were obtained with a Horiba Jobin Yvon T64000 spectrometer coupled with CCD camera and excited with an Ar^+ laser (line 514.12 nm). The surface morphology of the films was investigated by a TESCAN VEGA 5130 MM Scanning Electron Microscope (SEM). The optical transmittance spectra were measured with a spectrophotometer Jasco V-670. The resistivity, ρ (*T*), was measured at 300K using the van der Pauw method. The contacts were prepared by using a silver paste.

3 RESULTS AND DISCUSSION

The SEM image of the film surface (Figure 2) shows a homogenous coverage of the substrate at the major part. However, small inclusions are also observed. The XRF measurements were performed on at least nine points for each sample. The average composition values of the samples are shown in Table I. As it is seen, the composition is close to stoichiometry, however slight excess of Zn and Sn and lack of sulphur is observed for all samples.

Table I: Average values of XRF measurements of as-deposited Cu_2ZnSnS_4 thin films.

Sample	Cu(at.%)	Zn(at.%)	Sn(at.%)	S(at.%)
N090911-1	24.1	13.6	12.5	49.7
N120911-1	26.3	13.1	13.4	47.1
N120911-2	25.8	12.6	15.1	46.5
N120911-3	27.4	13.7	16.9	41.9

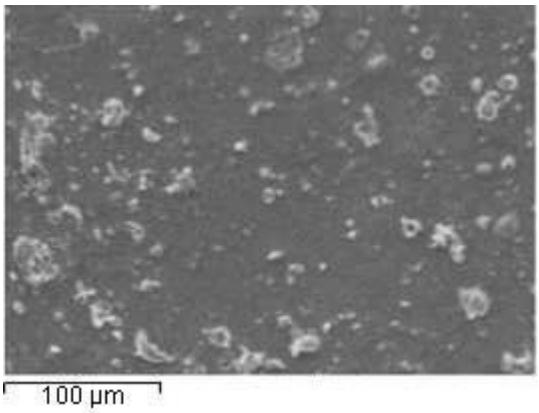

Figure 2: SEM image of the surface of as-deposited Cu_2ZnSnS_4 thin film.

For the as-deposited layers the GIXRD pattern (not shown) indicates the kesterite type phase with a = 5.419 Å and c = 10.871 Å as main phase. Small concentrations of secondary phases have also been detected. Figure 3 presents the Raman spectra of the as-deposited layer. The spectra show a dominant broad band at 337 cm^{-1} and a shoulder at 289 cm^{-1}, i.e. in the spectral region close to the frequency of the main A modes characteristic of CZTS [8, 9]. The shape of this band suggests a low crystalline quality of the as-deposited films. Presence of contributions from secondary phases as ZnS (main Raman mode at 350 cm^{-1} [10]), Cu_2SnS_3 (main Raman modes at 303 cm^{-1} and 356 cm^{-1} [11]) and Cu_3SnS_4 (main Raman mode at 318 cm^{-1} [8]) cannot be excluded, although the corresponding main Raman peaks cannot be resolved from the broad band.

As mentioned in Section 2, the annealing process was carried out in an evacuated volume with addition of

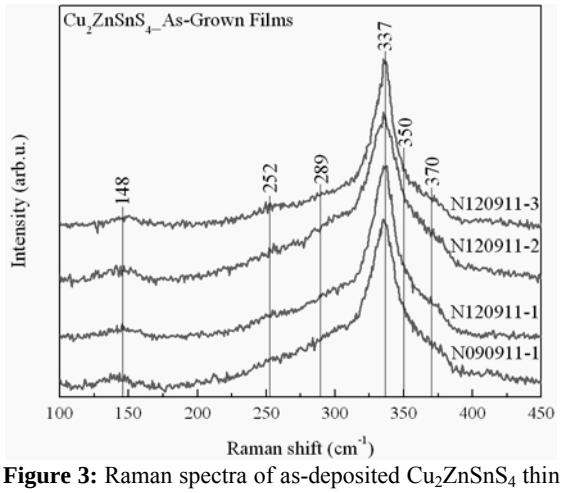

Figure 3: Raman spectra of as-deposited Cu_2ZnSnS_4 thin films.

elemental sulphur and tin, to avoid their re-evaporation during the annealing of the films. The average composition of the annealed films did not change significantly (see Table II). However, an increase of sulphur concentration and a decrease of both zinc and tin concentrations were observed. GIXRD patterns showed a reduction in the content of secondary phases and no structure type changes.

Table II: Average concentration values of the elements determined from XRF measurements of annealed Cu_2ZnSnS_4 thin films.

Sample	Cu(at.%)	Zn(at.%)	Sn(at.%)	S(at.%)
N090911-1	23.9	12.1	12.3	51.7
N120911-1	25.7	12.3	12.7	49.2
N120911-2	23.8	11.9	14.7	49.6
N120911-3	26.7	12.2	16.9	44.3

Raman spectra of the annealed thin films showed strong decrease of the width of the modes (see Figure 4), which yielded from a significant improvement of the crystalline quality of the samples. The Raman spectra are characterized by the main CZTS peaks at 337 cm^{-1} and 289 cm^{-1}, and weaker CZTS modes at 143 cm^{-1}, 168 cm^{-1}, 252 cm^{-1}, 350 cm^{-1} and 370 cm^{-1} [9]. The decrease in the width of the Raman peaks agrees also with the decrease in the content of secondary phases as suggested from GIXRD measurements, although in principle some contribution from ZnS mode at 350 cm^{-1} cannot be excluded.

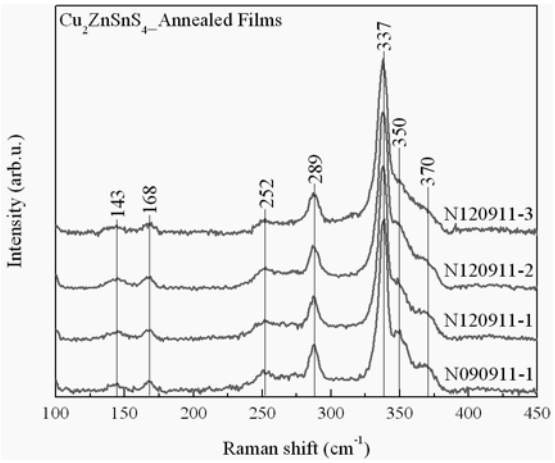

Figure 4: Raman spectra of annealed Cu_2ZnSnS_4 thin films.

The optical transmittance spectra were measured at 300K on thin film samples with the thickness *d* of about 1μm in the spectral range 500 – 900 nm. The absorption coefficient α was calculated from the measured transmittance through the relation $\alpha = (1/d)\ \ln(I_0/I) + \alpha R$ [12], where I_0 and I are the incident and transmitted radiation, respectively, and αR is a nearly constant residual absorption observed in the low-energy region of the spectra. Reflectivity was determined from the transmittance in the zero-absorption limit where it is expected that $T \approx (1 - R)/(1 + R)$ [12].

For direct band gap semiconductors,

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

where hν is the characteristic energy of a photon, and A is a temperature independent constant that depends on the effective mass and the refractive index. The $(\alpha h\nu)^2$ spectra (Fig. 5) show a linear dependence on photon energy over an appreciable energy range, revealing the existence of a direct band gap in the deposited films. Using the linear extrapolation method, the value of Eg is determined to 1.52 and 1.55 eV for the as-grown and annealed films, respectively. The Eg value is higher than that reported for CZTS films prepared by spray pyrolysis (1.40-1.45 eV [5]) and close to that of films fabricated by sequential deposition of metal elements and annealing in S flux (1.5 eV [2]).

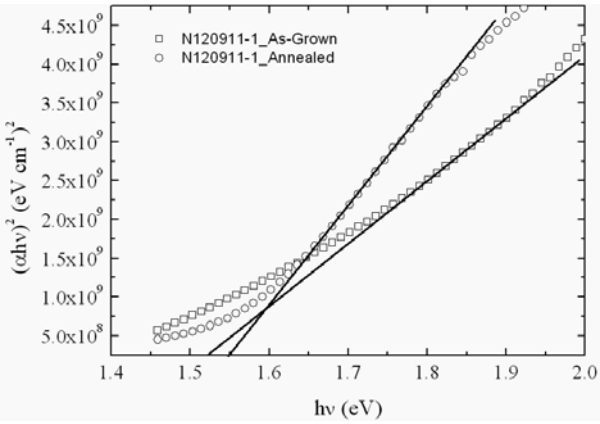

Figure 5. Plots $(\alpha h\nu)^2$ as a function of the photon energy of as-deposited and annealed CZTS films.

Room-temperature electrical resistivity of CZTS films was determined using van der Pauw technique. The films were found to be p-type and the resistivity was found to vary from $2*10^{-2}$ to $4.4*10^{-1}$ Ωcm and from $5*10^{-2}$ to $3.0*10^{-1}$ Ωcm for the as-deposited and annealed films, respectively. The data are in the same range as reported by Kumar et al. (from 0.02 to 2.00 Ωcm [5]) for CZTS films prepared by spray pyrolysis method.

4 CONCLUSIONS

Thin films of Cu_2ZnSnS_4 were deposited by spray pyrolysis method from solution of H_2O and C_2H_5OH with heightened concentration of pure chemical compounds at a substrate temperature of ~450 °C. The chemical composition of the as-prepared samples determined from XRF measurements was found to be close to stoichiometry. However, secondary phases and poor crystalline quality of the films was detected by GIXRD and RS measurements. After the annealing the crystalline quality was significantly improved and the contribution from secondary phases was considerably decreased. The direct band gap energy of the as-deposited CZTS thin films is 1.52 eV. The band gap of the annealed films increases up to 1.55 eV. The CZTS films showed good optical and suitable electrical properties for thin film solar cells.

5 ACKNOWLEDGMENTS

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6 REFERENCES

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