PREPARATION AND PROPERTIES OF CZTS THIN FILM PREPARED BY SPRAY PYROLYSIS

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Abstract: In this work we have developed thin-film CZTS (Cu_2ZnSnS_4) by "spray pyrolysis" technique on preheated glass substrates from an aqueous solution containing ions of copper, zinc, tin and sulfur at different temperatures. Then we performed structural analysis of samples prepared by different characterization methods such as X-ray diffraction (RXD), Raman microscopy, and transmission electron microscopy (SEM).
Experimental results have verified that the thin films deposited CZTS are relatively uniform on the substrates. Structural analysis by X-ray diffraction showed that the deposited films are Kestrite structure with a bias in the direction <112> with the appearance of a second phase the binary Cu_2-xS, which is confirmed by the analysis Raman spectroscopy.

Keywords: Spray pyrolysis, CZTS, Solar cell, absorber, Characterization.

I. Introduction

The photovoltaic cell is a priori one of the best ways to convert directly sunlight into electricity. The development of photovoltaic energy requires significant technological research efforts on the use of new processes and materials at low cost and good performance.
Chains of thin film materials such as CIS, CIGS and CZTS become promoters for the structure of transparent solar cells / buffer / absorber / metal.
Cu_2ZnSnS_4 (CZTS) is a semiconductor absorber for the most promising thin film solar cells and thus for a cheap solar cells. It's characterized by an energy gap between 1.45 eV and 1.6 eV, an absorption coefficient of $10^4 cm^{-1}$[1] order. The crystal structure of CZTS is similar to the chalcopyrite semiconductor CIGS [$Cu(Ga,In)Se_2$, $Cu(Ga,In)S_2$], which is currently considered as the most promising absorbent layers in terms of their highest efficiency photovoltaic conversion 19.9% [2]. However, the components of CIGS are expensive (In, Ga) and toxic (Se). In contrast CZTS (Cu2ZnSnS4) is a quaternary compound formed by non-toxic and abundant matters.
Several deposition techniques have been used for CZTS thin film manufacture, such as laser ablation [3], RF magnetron sputtering [4], co-evaporation [5-6], electrodeposition [7], sol- gel [8], spray pyrolysis [9-10], etc... In this work we have developed thin-film CZTS by atomic pulverization technique called "spray pyrolysis", the latter has found great success in recent years since it become an integral part in the industrial process for the cell's preparation at large scales, these CZTS thin layers are placed on preheated glass substrates from an aqueous solution containing copper ions, zinc, tin and sulfur at different temperatures. The structural, electrical and optical films were analyzed by X-ray diffraction (RXD) and scanning electron microscopy (SEM).

II.Experimental studies

The CZTS thin films were filed by the spray pyrolysis technique on glass substrates at 375 °C and 425 °C temperatures and deposition time of 60 min. Glass substrates were washed with HNO_3 and then rinsed with disionised water, ethanol and acetone. The thin layers of CZTS are prepared from an aqueous solution containing copper chloride $CuCl_2$ (0.01 M), zinc acetate dihydrate Zn $(CH_3COO)_2.2H_2O$ (0.005 M), tin chloride $SnCl_2$ dihydrate (0.005 M) and Theoria (0.04 M) as a source of sulfur. The solution was sprayed at flow rates [1 ml / min] with the compressed air flow of 3.5 bars. The nozzle-substrate distance was fixed at 30 cm. The spraying was done on ordinary glass substrates preheated.
Structural characterization of the sample was carried out by an X-ray diffractometer (XPERT-PR) at high resolution with a Cu anti-cathode copper over an interval of [20 ° 60 °]. The microstructure and surface morphology were observed by scanning electron microscopy (SEM). The chemical elemental composition was determined by EDX (Energy Dispersive Spectrometer) system attached to SEM.

III.Results and discussion

3.1. Structure and morphology

a) Structural properties (XRD)

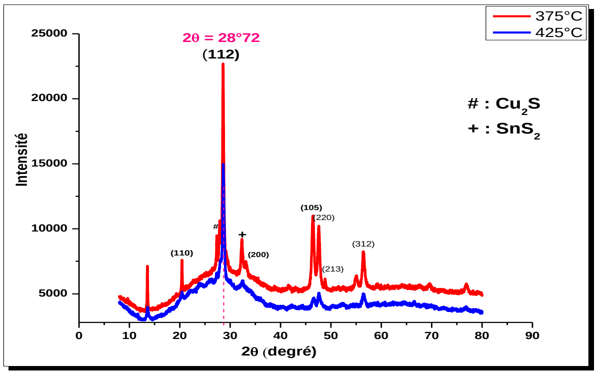

Fig.1. XRD pattern of CZTS samples prepared at different temperature.

Figure 1 shows the X-ray diffraction's spectra for CZTS thin film developed at different temperatures. XRD spectrum's peaks indicate that all obtained films are polycrystalline with a Kestrite structure in a preferred orientation along the direction <112> located. The most intense peak was observed for the samples prepared under the following conditions: T=375°C, Q=1mL/min, we can see an emergence of a bit strange (Cu_2S) [11] which is confirmed by Raman microscopy.

b) Microstructure (MEB)

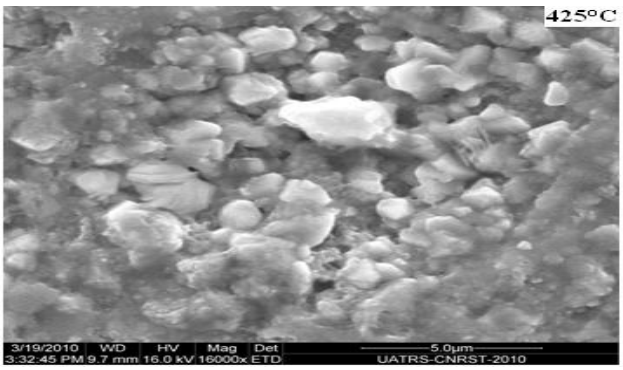

Fig.2. SEM image of CZTS samples prepared at 425°C

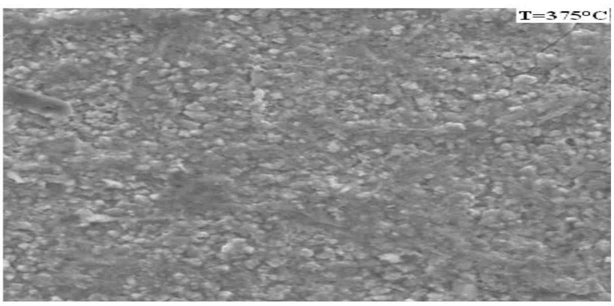

Fig.3. Elementary composition of CZTS for different temperature (375°C and 425°C)

• The picture of the sample prepared at 375 °C shows that there is material in the form of grains condensed, compact and homogeneous. This allows us to see that the structure is uniformly smooth.
• The sample prepared at 400 °C, allow us to see that there is a lot of material deposited on the substrate but their structure is inhomogeneous.

c) Chemical Composition (EDS)

The elemental analysis by EDS of CZTS samples showed a deficiency of sulfur and tin to high temperatures, therefore a considerable deviation of the stoichiometry (Table 1), sulfur deficiency is significant, since it is volatile.

Samples	Elemental compositions (at%)				Report Compositions	
	Cu	Zn	Sn	S	Zn/Sn	Cu/(Zn+Sn)
At 425°C	37,92	19,86	6,39	38,5	3	1,44
At 375°C	37,73	19,19	12,55	30,55	1,52	1,18

Fig.4. Elementary composition of CZTS for different temperature (375°C and 425°C)

3.2. Raman spectroscopy optical properties

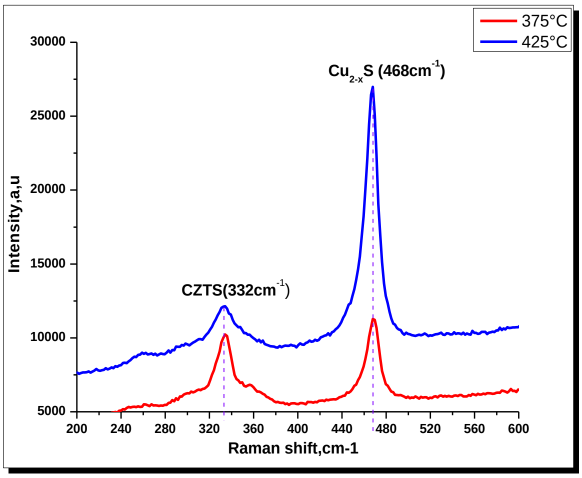

Fig.5.Raman spectra of thin CZTS for T = 425°C and 375°C.

Figure 5 shows the existence of a secondary phase of the binary Cu2-x S which is comparable with the results of X-ray diffraction (Figure 1) published by the research work [11-12]. The appearance of this strange phase on the layer's outer surface is due to evaporation of sulfur (volatile component) at high temperature (425 ° C) Figure 4.

IV. Conclusion

• The X-ray diffraction's spectra (XRD) indicate that all the films obtained are polycrystalline with a Kestrite structure with a preferred orientation along the <112> direction.
• The most intense peak was observed for the samples prepared under the following conditions: T = 375 ° C, Q = 1mL/min.
• The appearance of a bit strange (Cu_2S) by X-ray diffraction (XRD) is comparable with the results of spectroscopy Raman and those published by other authors.
• The elemental composition (EDX) showed a deficiency in the tin and sulfur.

V. References

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