

Comparative study between CZTS and CZTSe thin layers for photovoltaic applications

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Abstract

A comparative study of the thin layer based on copper zinc tin sulphide $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and that based on copper zinc tin selenide $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) was made in order to assess the structural, morphological, optical and electrical qualities. for better use in improving performance of CZTS, CZTSe or CZTSSe based solar cell. CZTS and CZTSe thin films prepared by the spray pyrolysis technique were characterized by X-ray diffraction (XRD) which confirmed their kesterite structure in the tetragonal crystal phase. In addition, the analysis of the surfaces of the thin layers with the scanning electron microscope SEM, showed compact grains, well agglomerated and of appreciable sizes. UV-visible spectroscopy measured the quality of light absorption and located the bandgap energy values between 1.16 eV for CZTSe and 1.69 eV for CZTS i.e. in the range of potential absorbers for CZTS and CZTSe based thin film solar cells.

Keywords : CZTS, CZTSe, SEM, solar cells, Spray pyrolysis, XRD.

Introduction

The strong and rapid global growth in fossil fuel consumption has sparked interest in alternative and renewable sources. Among them, solar energy appears to be the cleanest and most abundant. Its conversion into electricity requires semiconductor materials that form the photovoltaic cell. Apart from silicon, which still dominates the market, more promising, abundant and less expensive materials are attracting attention [1,2].

The quaternary kesterite materials CZTS, CZTSe and CZTSSe have the advantage of being made up of elements abundant on earth, less expensive, respectful of the environment, and also have semi-conducting qualities such as a coefficient of high absorption (of the order of 10^4 cm^{-1}), a direct and adjustable band gap (from 1 to 1.5 eV) and are intrinsic p-type semiconductors [3,4]. Their uses in thin-film photovoltaic technology promise much hope although their current electrical conversion power does not exceed 13%. This low performance is mainly due to the existence of many defects during the formation of the material, the crystallization process, which multiplies the recombinations and alters the open circuit voltage of the cell. Several techniques, generally in two steps, are used for the fabrication of thin layers of CZTS and CZTSe: the deposition of cationic precursors followed by annealing in a sulfur and/or a selenium environment. Methods vary from vacuum deposition techniques such as sputtering, evaporation, and pulsed laser deposition, to chemical-based non-vacuum deposition techniques such as electrodeposition, hydrazine-based solution, and sol-gel base [5].

In this work, kesterite thin-films of CZTS and CZTSe were deposited by spray pyrolysis, a simple and low cost method suitable for large-scale production and allowing easy control of substrate temperature, coating rate by choosing optimal concentrations of the molecular precursor.

The samples as-obtained were annealed in a sulfur atmosphere for the CZTS and selenized for the CZTSe, then characterized. The crystal and phase formation of the obtained thin-films was analyzed by X-ray diffraction (XRD). The

optical properties were studied by ultraviolet–visible spectroscopy (UV–Vis). The surface morphology of the thin-films was analyzed by scanning electron microscope (SEM).

Experimental part

We used soda-lime glass substrates of dimensions 25x25 mm², 2.2 mm thick, coated with a thin layer of 600 nm thickness of FTO as metallic transparent conductive oxide. First of all, the FTO-coated glasses were cleaned under ultrasound in distilled water with liquid soap, then in ethanol and in acetone. Finally, any residual trace of organic matter is eliminated by UV Ozone treatment.

CZTS and CZTSe precursor solutions were prepared from the dissolution of 90 mM anhydrous copper chloride (CuCl₂, Riedel-de Haen), 63 mM zinc chloride (ZnCl₂, Fulka), 50 mM doubly hydrated tin (SnCl₂ · 2H₂O) and thiourea (SC(NH₂)₂, Fulka) as source of sulfide anion and selenic acid SeO₃H₂ as source of selenide ion.

The plate and the FTO-coated glass substrats are preheated to 380° C. for 30 min. The spray device makes it possible to propel fine drops of the precursor solution by compressed air under a pressure of 1.2 bar at a distance of 30 cm. During spraying, temperature is maintained at 380°C. The samples as-formed remain at this temperature for 30 min on the plate before slowly cooling to room temperature. The process of spray followed by annealing is schematized in figure 1.

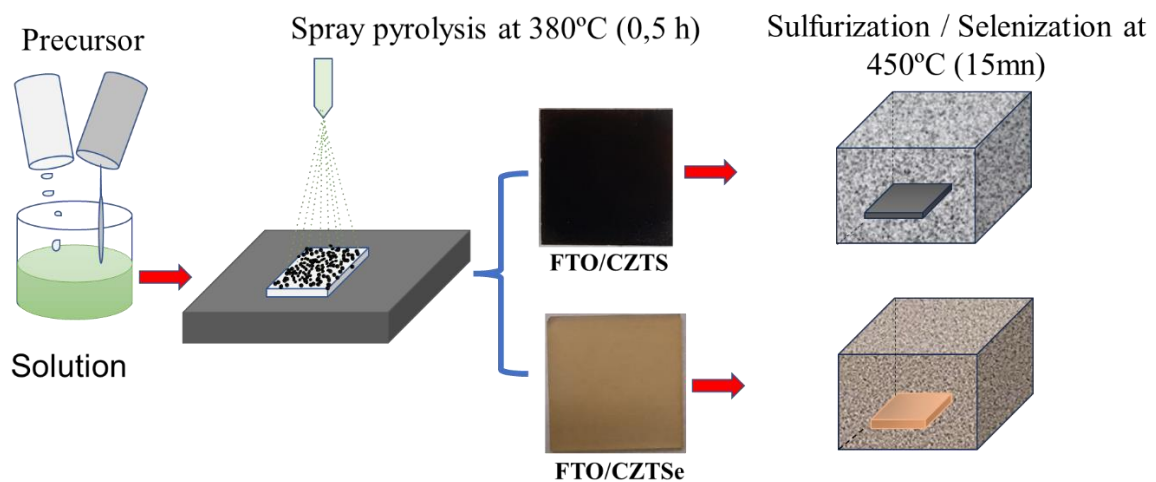


Fig. 1 : Spray pyrolysis and annealed process

The X-ray diffraction (XRD) analysis were performed to determine the crystal phases of the deposited thin-films using the RIGAKU Ultima IV diffractometer with Cu-K α radiation at the wavelength λ of 1.5406 Å. Figure 2 shows the XRD pattern (a) and the variation of FWHM and grain size (b) of the obtained CZTS and CZTSe samples.

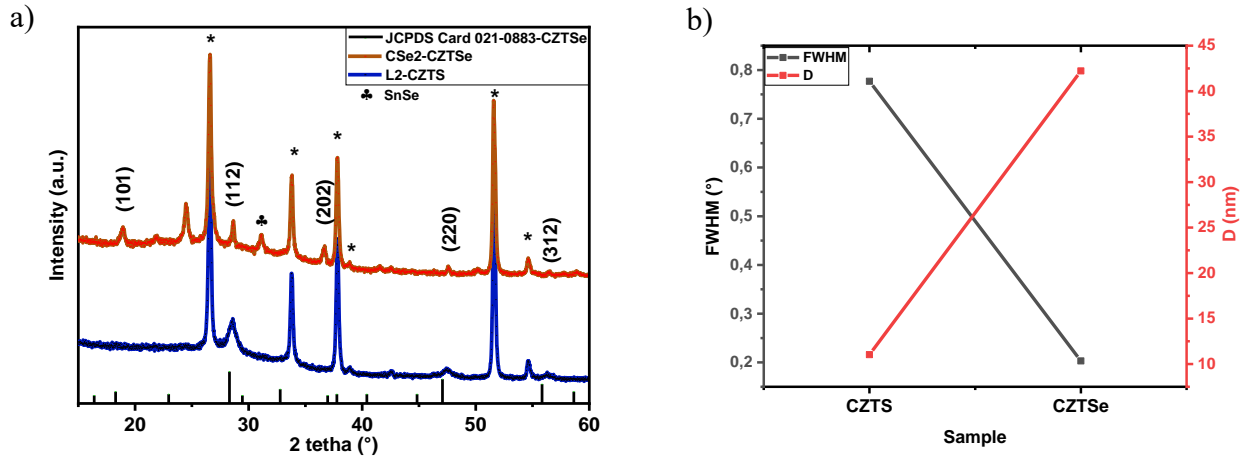


Fig. 2 : XRD pattern (a), Full Width at Half Maximum (FWHM) and grain size variation (b) of as-deposited CZTS and CZTSe .

The X-ray diffraction pattern of the two samples indicate the different characteristic 2θ peaks: 28.7° , 47.6° and 56.4° corresponding to (112), (220) and (312) planes respectively and which are attributed to the kesterite structure according to JCPDS card no. 021-0883 [6]. The presence of complementary peaks (101), (202) located at angles 2θ : 18.9° and 36.6° respectively for CZTSe indicates a notable difference in crystallinity between CZTS and CZTSe. In addition, the grain size increases and the FWHM decreases when switching from CZTS to CZTSe.

SEM images show a good agglomeration of the grains for the two types of obtained samples, denser and with larger grain sizes for the CZTSe (figure 3(a) and 3(b)).

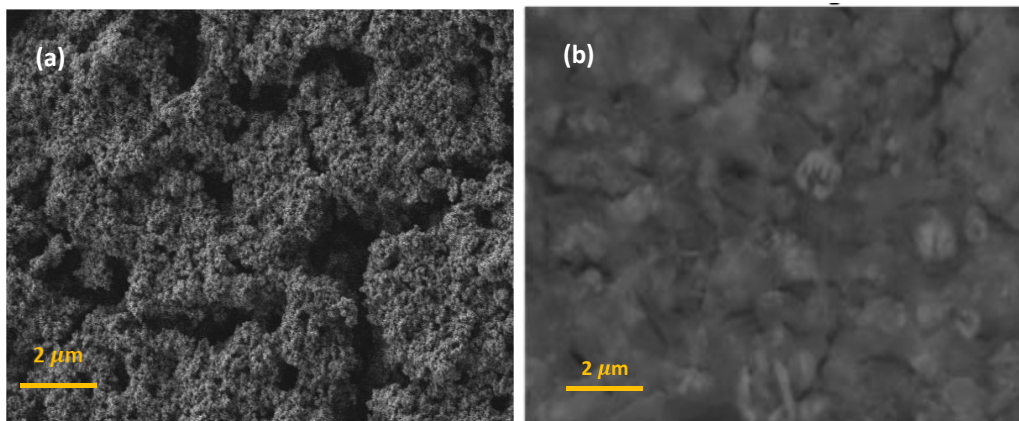


Fig. 3 : SEM image of CZTS (a) and CZTSe (b) by spray pyrolysis

The optical properties of two materials prepared by spray pyrolysis are investigated. Optical absorption spectrum of CZTS and CZTSe thin films were produced by UV-visible spectrophotometer and the band gap was estimated using Tauc's plot. Figure 4 shows thin films of CZTS and CZTSe which absorb in the visible with respective band gaps of 1.69 eV and 1.16 eV when annealed at 450°C in the presence of sulfur and selenium.

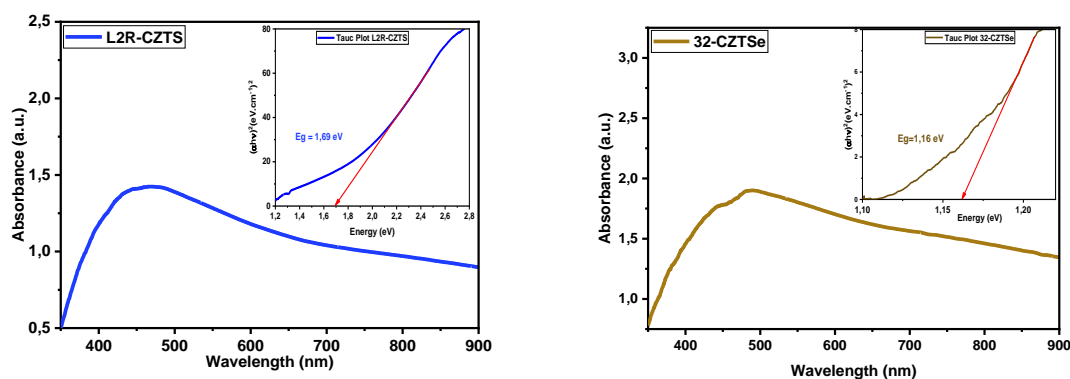


Fig. 4 : Absorption spectrum of CZTS and CZTSe thin films

Conclusion

The copper zinc tin sulphide $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and copper zinc tin selenide $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) show good structural, morphological, optical and electrical properties. CZTS and CZTSe thin films prepared by the spray pyrolysis technique confirmed their kesterite structure in the tetragonal crystal phase. In addition, the SEM analysis of the surfaces of the thin layers showed compact grains, well agglomerated and of high grain sizes. The bandgap energy values between 1.16 eV for CZTSe and 1.69 eV for CZTS i.e. where make the CZTS and CZTSe as good absorber for CZTS based thin film solar cells.

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