XPS study for CZTS thin films growth by PVD co-evaporation method

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Abstract. This study shows the preparation of different Cu_2ZnSnS_4 thin films, following the co-evaporation route of metals (Cu, Sn and Zn Zn) in sulfur atmosphere, in three steps sulfide formation. The best results were acquired by Cu/Sn/Zn sequence which has single kesterite phase according to XRD characterization. The surface analyses by X-ray photoelectron spectroscopy (XPS) of Cu_2ZnSnS_4 polycrystalline thin film growth with sequence Cu/Sn/Zn were studied. Binding energies at 161.5 eV, 486.1 eV, 932.4 eV and 1021.6 eV were found for S $2p_{3/2}$, Sn $3d_{5/2}$, Cu $2p_{3/2}$ and Zn $2p_{3/2}$ respectively. SEM and EDS analyses show the morphology and elemental composition of Kesterite CZTS with Sn looses giving a Cu poor and Zn rich structure. The solar cell efficiencies were $\eta = 1.6\%$ for Mo/CZTS/CdS/ZnS/ITO device and $\eta = 1.2\%$ for Mo/CZTS/CdS/ZnS/ITO device, using Cu/Sn/Zn evaporation sequence. These results show the growing use of CZTS kesterite semiconducting material as absorber layer in solar cell devices fabricated by thin film technology.

Resumen. Este estudio muestra la preparación de diferentes películas delgadas de Cu_2ZnSnS_4, por medio de la coevaporación de metales (Cu, Sn and Zn) en atmósferas de azufre, y en tres pasos de formación de sulfuro. Los mejores resultados se obtuvieron mediante la secuencia Cu/Sn/Zn, la cual tiene una sola fase kesterita, de acuerdo con la caracterización XRD. Se realizaron análisis de la superficie por medio de una espectroscopia de fotoelectrones emitidos por rayos X (XPS) sobre el crecimiento de películas policristalinas delgadas Cu_2ZnSnS_4, con una secuencia Cu/Sn/Zn. Se encontraron energías de enlace nuclear de 161.5 eV, 486.1 eV, 932.4 eV y 1021.6 eV para S $2p_{3/2}$, Sn $3d_{5/2}$, Cu $2p_{3/2}$ y Zn $2p_{3/2}$, respectivamente. Los análisis SEM y EDS muestran la morfología y la composición elemental de la Kesterita CZTS con pérdidas Sn, resultando en una estructura pobre en Cu y rica en Zn. Las eficiencias de las celdas solares fueron de $\eta = 1.6\%$ para un dispositivo Mo/CZTS/CdS/ZnS/ITO y de $\eta = 1.2\%$ para un dispositivo Mo/CZTS/CdS/ZnS/ITO, usando la secuencia de evaporación Cu/Sn/Zn. Estos resultados demuestran el crecimiento en el uso del material semiconductor kesterita CZTS como una película

absorbente en dispositivos de celdas solares fabricados por medio de una tecnología de películas delgadas.

Keywords: X-ray photoelectron spectroscopy, Cu_2ZnSnS_4, EDS, XRD.

Palabras Clave: espectroscopio de foto-electrones emitidos por rayos X, Cu_2ZnSnS_4, EDS, XRD.

1. Introduction

The family of CIGSSe semiconducting compounds have been the most studied materials for solar cells by thin film technology during last 30 years [1,2]. Despite of this, there is a new scientific and technical way to produce absorber layers without expensive, strategic and heavy metals such In and Ga. Sn and Zn are crust abundant elements and also cheap to isolate and purificate them [3]. Zn^{2+} and Sn^{4+} can replace In or Ga in order to change the chalcopyrit by kesterite phase and maintain the tetragonal unit cell without significant changes on lattice parameters [4].

Several synthesis and growth techniques have been used to produce Cu_2ZnSnS_4 semiconducting material such as pulsed laser deposition (PLD) [5], colloidal [6], high temperature and HV ampoule [7], electrochemistry [8] spray [9] and chemical wet method [10], but in this work has been used co-evaporation technique by physical vapor deposition. PVD co-evaporation technique allows evaporate the precursor metals in presence of S_2 in order to obtain the quaternary CZTS compound trough sulfide sequential reactions. Efficiency close to 10% was achieved by IBM [11,12], in this work the efficiency were 1.6% for Mo/CZTS/CdS/ZnS/ITO structure and 1.2% for Mo/CZTS/CdS/ZnS/ITO structure, using Cu/Sn/Zn evaporation sequence as absorber layer.

2. Experimental

CZTS Thin films of 600 nm in thickness were prepared by PVD co-evaporation process. The growth process was carried out in three steps in order to obtain in each of them a thermo stable sulfide that can react between them to form Cu_2ZnSnS_4.

If the process starts with Cu evaporation in presence of S_2 is obtained Cu_2S, in the second step is evaporated Sn to produced the SnS_2 which reacts with Cu_2S to obtain Cu_2SnS_3, and finally, in the third step is evaporated Zn to form ZnS which reacts with Cu_2SnS_3 to form Cu_2SnZnS_4, this method avoid secondary phase formation due to ramification reactions, if is used the correct metal amount. However, were prepared the 6 possible sequences (Cu/Sn/Zn), (Cu/Zn/Sn), (Sn/Zn/Cu), (Sn/Cu/Zn), (Zn/Sn/Cu) and (Zn/Cu/Sn) in order to identify secondary phase formation and crystallographic properties (Fig. 1). According to XRD analyses Cu/Sn/Zn sequence is single phase kesterite type structure. This sequence is used for the whole characterization and as absorber layer in the built solar cell device.

In (Fig. 2) is shown the temperature ramp and the evaporation rate in the CZTS growth process. Temperature substrate is one of the most important parameters in the synthesis process, then the temperatures substrate to obtain the above mentioned phases were 600 °C, 250 °C and 600 °C for Cu, Sn and Zn respectively. High vacuum at 1×10^{-5} mbar is required and quartz crystals microbalance is used for determine the metal evaporation rate in each evaporation moment. X-ray diffraction XRD analyses were performed and the sequence Cu/Sn/Zn shows the single phase formation kesterite type tetragonal structure being p-type semiconducting material. Energy dispersive X-ray spectroscopy EDS technique was used to identify the elemental composition of Cu/Sn/Zn sequence sample.

Structural characterization was carried out by *LABX XRD 6000. Shimadzu* equipment with Cu Kα radiation between 10° - 70° in 2θ sweep rate 2°/min, step width 0.02° and voltage 40 kV. SEM measures were carried out with a FeiQuanta 200 electron microscope in high vacuum mode using an Everhart-Thorney detector (30 kV) attached with a EDS probe to identify grain size, morphological shape and elemental compositional analysis. The elemental composition analysis of the CZTS thin films was analyzed using an X-ray photoelectron spectrometer (K-Alpha, Thermo VG Scientific, UK) with a multi-channel detector, which can withstand high photonic energies from 0.1 to 3 keV. The whole cells were completed with ZnS [13] and CdS [14] by chemical bath deposition process, ZnO thin film was growth by RF sputtering technique, ITO top contact layer by Magnetron sputtering and Mo back contact with sputtering RF. Characteristic I-V curve was performed by solar simulation equipment in standard conditions AM 1.5, under 100 mW/cm^2 illumination (measured with a calibrated solar cell) and normal position.

3. Results

The relative atomic concentrations of Zn, Cu, Sn and S were determined from high-resolution XPS core level spectra integrated peak areas. (Fig. 3) shows the Zn $L_3M_{45}M_{45}$ Auger peak at BE = 496.3 eV (KE = 990.4 eV) can be observed on the high energy side of the Sn 3d core level spectrum.

According to the XPS spectra of Cu_2ZnSnS_4 thin films, the binding energies (BE) of Zn $2p_{3/2}$ (Fig. 4), Cu $2p_{3/2}$ (Fig. 5), Sn $3d_{5/2}$, and S $2p_{3/2}$ (Fig. 6), core levels after surface cleaning are located at 1021.6 eV, 932.4 eV, 486.1 eV, and 161.5 eV respectively. These results suggest that samples with Cu/Sn/Zn sequence do not have secondary phase formation.

The EDS analysis (Fig. 7) shows the distribution of constituent elements in the crystals was homogeneous and the bulk composition of the analyzed material was: [Cu] = 23.12; [Zn] = 16.83; [Sn] = 10.95; and [S] = 49.09 mol% giving the following concentration ratios: Cu/(Zn+Sn) = 0.83 and Zn/Sn = 1.53. The kesterite phase of the Cu_2ZnSnS_4 with Cu/Sn/Zn sequence thin film was confirmed by XRD measurements. (Fig. 8) shows the grain size for CZTS Cu/Sn/Zn sequence.

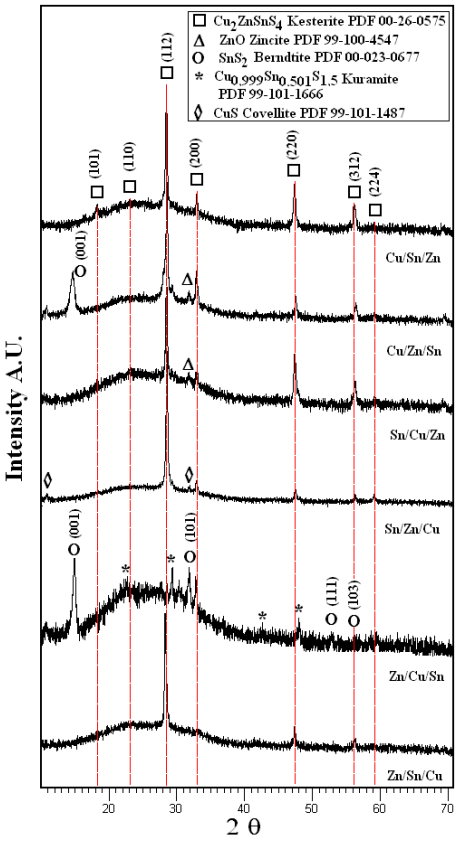

Fig. 1. X-Ray diffraction patterns of typical CZTS thin films deposited varying the sequence (Cu/Zn/Sn, Cu/Sn/Zn, Sn/Cu/Zn, Sn/Zn/Cu, Zn/Cu/Sn, and Zn/Sn/Cu).

(Fig. 9) shows the solar cell using CdS as buffer layer. The efficiency for this solar device was $\eta = 1.2\%$. (Fig. 10) shows the solar cell using ZnS as buffer layer with an efficiency of $\eta = 1.6\%$. The energy loses in the built cells must be due to the low thickness of CZTS absorber layer and passivation due to MoS_2 formation. These results suggest that the Cu/Zn/Sn evaporation sequence starting from metal precursors in S_2 atmosphere leads a single kesterite phase which has adequate structural, morphological and chemical properties to be used as absorber layer in solar cell devices by thin film technology.

4. Conclusions

EDS analysis show atomic composition S: 49.09%, Cu: 23.12%, Zn: 16.83% and Sn: 10.95%. The absence of the Auger peak Sn $M_4N_{45}N_{45}$ of CZTS thin films

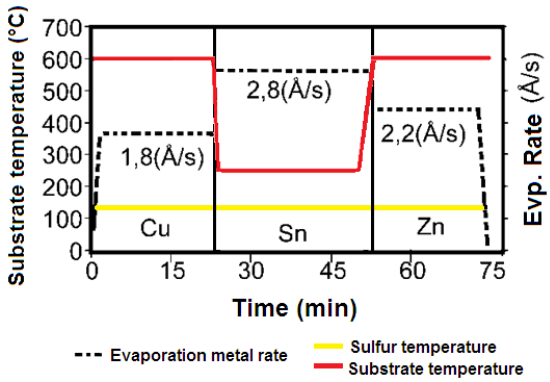

Fig. 2. Substrate temperature ramp and evaporation metal rate in a co-evaporation process with sequence Cu/Sn/Zn. Sulfur temperature is keeping constant at 140 °C during all process.

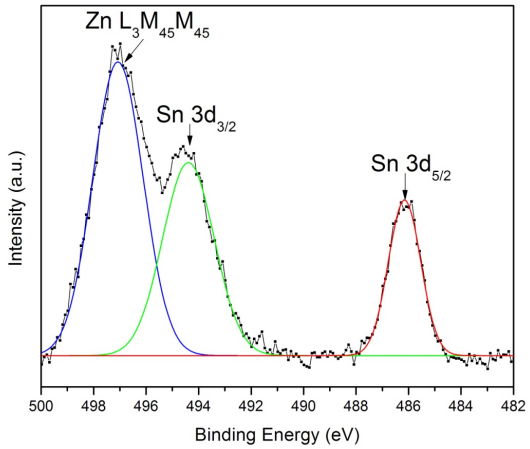

Fig. 3. High-resolution XPS spectra of the Sn 3d core level and Auger peak the Zn $L_3M_{45}M_{45}$ of CZTS thin film.

suggests non Sn_xS_y phase on the top of the surface, this results is according to the EDS tin analysis, it leads to a tetragonal kesterite structure Cu-reach and Zn-poor. The absence of chemical shifts in the found XPS signals core levels, suggest no satellite signals. Characterization performed by XRD gave evidence of the formation of single phase CZTS films with Kesterite structure using optimized growth parameters; however the chosen sequence in which the metallic precursors

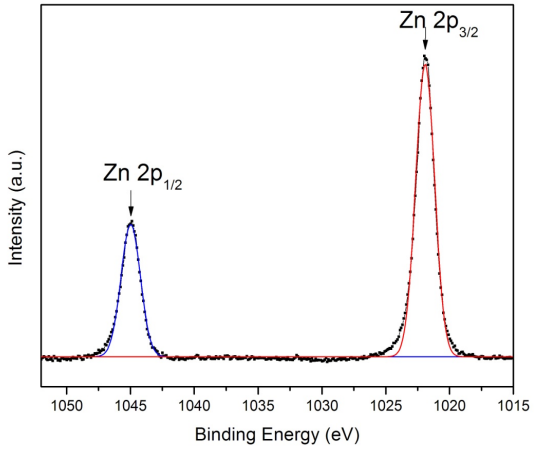

Fig. 4. High-resolution XPS spectra of the Zn 2p core level of CZTS thin film.

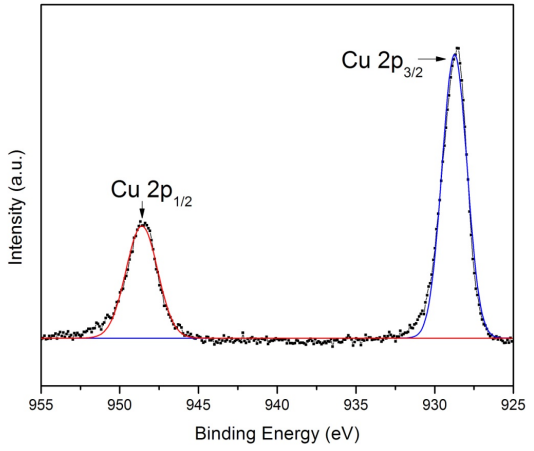

Fig. 5. High-resolution XPS spectra of the Cu 2p core level of CZTS thin film.

are evaporated, significantly affects the phase, morphology, as well as, structural properties of the CZTS films. The poor crystallographic qualities of CZTS thin films are probably associated to structural and native defects.

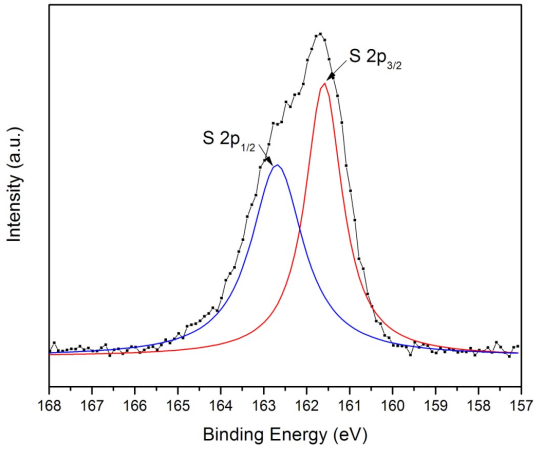

Fig. 6. High-resolution XPS spectra of the S 2p core level of CZTS thin film.

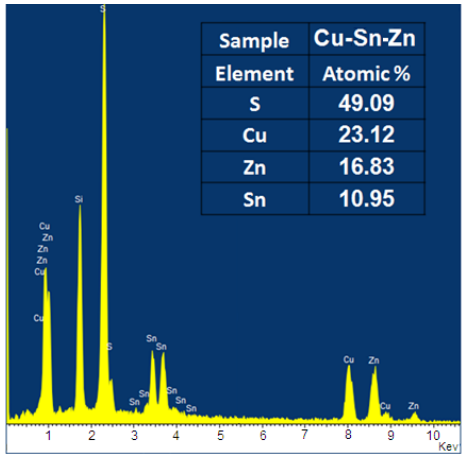

Fig. 7. EDS analysis for co-evaporation sequence Cu/Sn/Zn.

Solar cell efficiency was $\eta = 1.6\%$ for SLG/Mo/CZTS/CdS/ZnO/ITO device and $\eta = 1.2\%$ for SLG/Mo/CZTS/ZnS/ZnO/ITO, those results suggest that ZnS can be replaced CdS as buffer layer in low cost solar cell devices.

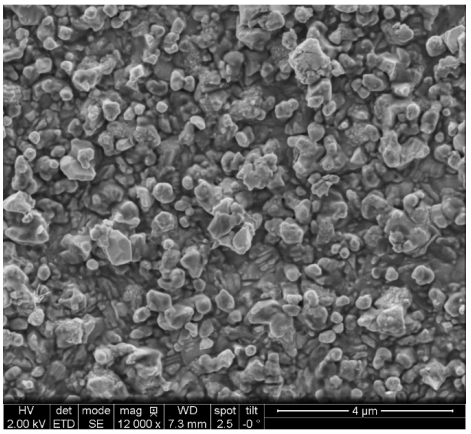

Fig. 8. SEM image for CZTS with sequence co-evaporation Cu/Sn/Zn.

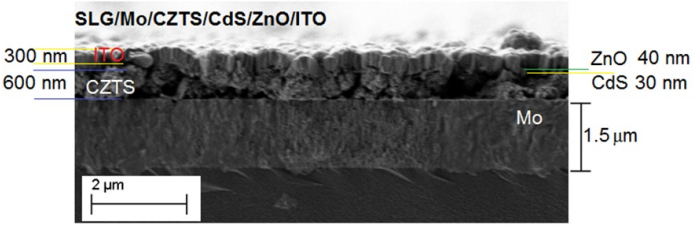

Fig. 9. Cross section of SLG/Mo/CZTS/CdS/ZnO/ITO solar cell device.

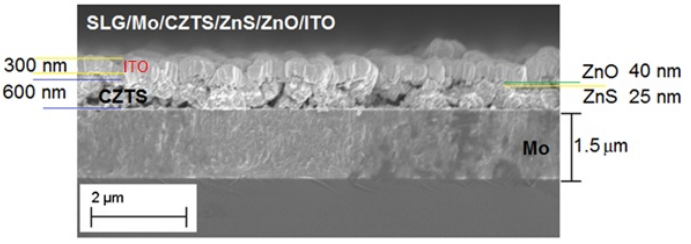

Fig. 10. Cross section image of SLG/Mo/CZTS/ZnS/ZnO/ITO solar cell device.

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