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COMPOSITIONAL STUDY OF Cu_2ZnSnS_4 ABSORBER LAYERS FOR PHOTOVOLTAIC SOLAR CELL DEVICES

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ABSTRACT

The surface analyses by X-ray photoelectron spectroscopy (XPS) of Cu_2ZnSnS_4 polycrystalline of thin film growth using physical vapor deposition (PVD) starting from metallic precursor in atmosphere of S_2, 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 EDAX analyses show the morphology and elemental composition of Kesterite CZTS with Sn looses giving a Cu poor and Zn rich structure.

Keywords: *X-ray photoelectron spectroscopy, Timing analysis, Cu_2ZnSnS_4, EDAX*

RESUMEN

El análisis de superficie por (XPS) Espectroscopia Fotoelectrónica de Rayos-x de películas delgadas policristalinas del compuesto Cu_2ZnSnS_4 fueron sintetizadas empleando la técnica (PVD) Physical Vapor Deposition, partiendo de los precursores metálicos en atmosfera de Azufre en un proceso de co-evaporación de tres etapas. Las energías de enlace a 161.5 eV, 486.1 eV, 932.4 eV y 1021.6 eV fueron encontradas para S $2p_{3/2}$, Sn $3d_{5/2}$, Cu $2p_{3/2}$ y Zn $2p_{3/2}$ respectivamente. Los análisis SEM y EDAX dan evidencia de la morfología y la composición elemental de la fase Kesterita CZTS con pérdidas de Sn reflejándose en una composición global pobre en Cu y rica en Zn.

Palabras Clave: *Espectroscopia fotoelectrónica de rayos X, Cu_2ZnSnS_4, EDAX*

1 INTRODUCTION

The family of CIGSSe semiconducting compounds have been the most studied materials for solar cell by thin film technology during last 30 years [1,2]. Despite of this, there is a new scientific and technical way to produce absorbent 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_2SnZnS_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 10.0% 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.

2 EXPERIMENTAL

CZTS Thin films of 600 nm in thickness were prepared by co-evaporation PVD 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 produced the SnS_2 which reacts with Cu_2S to obtain Cu_2SnS_3 and in the third step is evaporated Zn to form ZnS which reacts with Cu_2SnS_3 to form Cu_2ZnSnS_4, this method avoid secondary phase formation due to ramification reactions. In figure 1 is showing the temperature ramp and the evaporation rate in the CZTS growth process. Temperature substrate is one of the most important parameters in the synthesis, then the temperatures substrate are 600°C, 250°C and 600°C for Cu, Sn and Zn respectively. High vacuum at $1X10^{-5}$ mbar is required and quartz crystals micro-balance is used for determine the metal evaporation rate in each evaporation moment. 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 (EDAX) was measured to identify the elemental composition of Cu/Sn/Zn sequence simple.

3 RESULTS

The results are show in figures 1 to 7. According to the XPS spectra of Cu_2ZnSnS_4 thin films, the binding energies (BE) of Zn $2p_{3/2}$, $Cu2p_{3/2}$,$Sn3d_{5/2}$, and $S2p_{3/2}$ core levels after surface cleaning are located at 1021.6 eV, 932.4 eV, 486.1 eV, 161.5 eV, and 53.9 eV, respectively.

Oxygen and carbon contamination is typically due to the humidity and sample storage in a plastic vessel at atmospheric conditions. 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.

The relative atomic concentrations of Zn, Cu, Sn and S were determined from high-resolution XPS core level spectra integrated peak areas. The EDX analysis showed that the distribution of constituent elements in the crystals was homogeneous and the bulk composition of the analysed material was: [Cu]=23.2; [Zn]=13,0; [Sn]=12.7; [Se]=15,0 and [S]=36.1 mol% giving the following concentration ratios: Cu/(Zn+Sn)=0.90 and Zn/Sn=1.02. The kesterite phase of the Cu_2ZnSnS_4 with Cu/Sn/Zn sequence thin film was confirmed by XRD measurements.

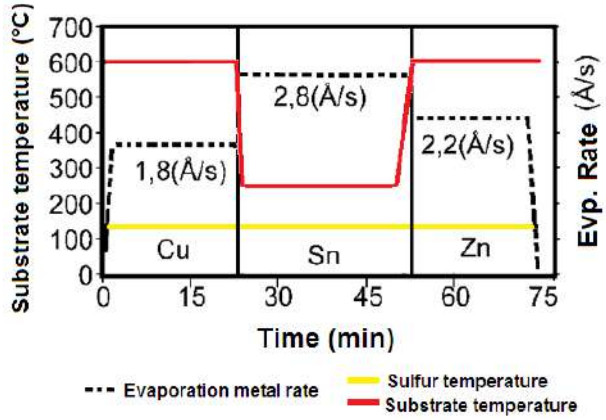

Figure 1. Substrate temperature ramp and evaporation metal rate in a co-evaporation process with sequence Cu/Sn/Zn. Sulfur temperature keep constant at 140 °C during all process.

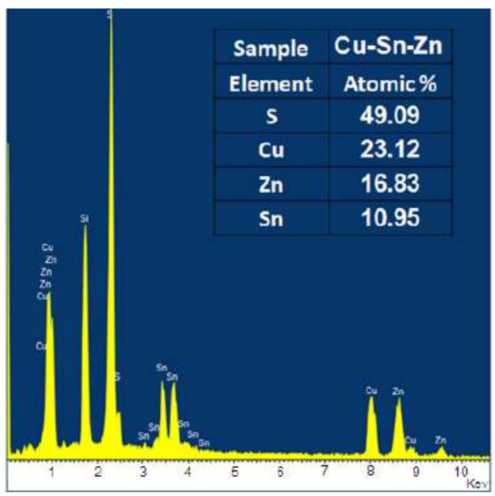

Figure 2. EDAX analysis for co-evaporation sequence Cu/Sn/Zn

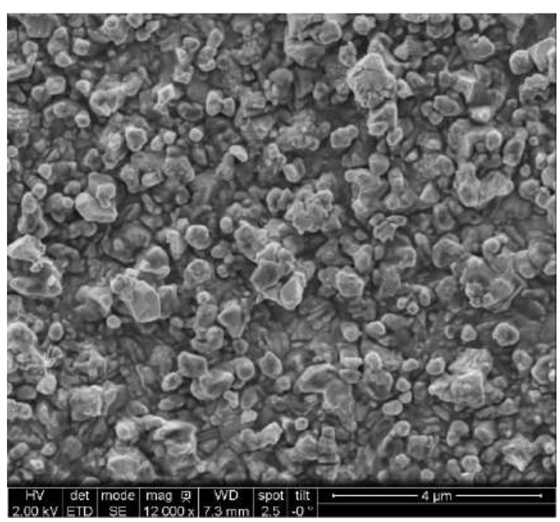

Figure 3. SEM image for CZTS with sequence co-evaporation Cu/Sn/Zn

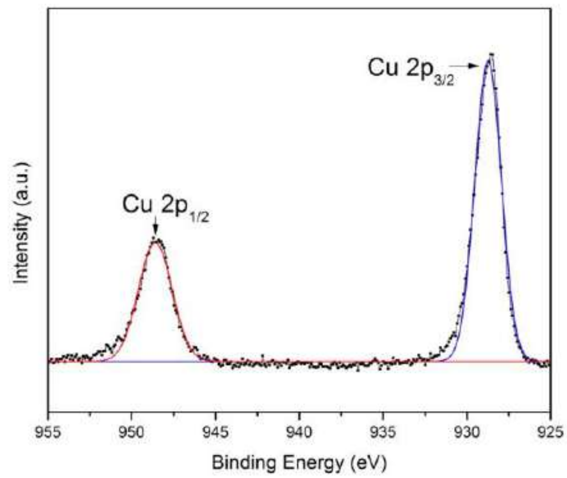

Figure 4. High-resolution XPS spectra of the Cu 2p core level of CZTS thin film.

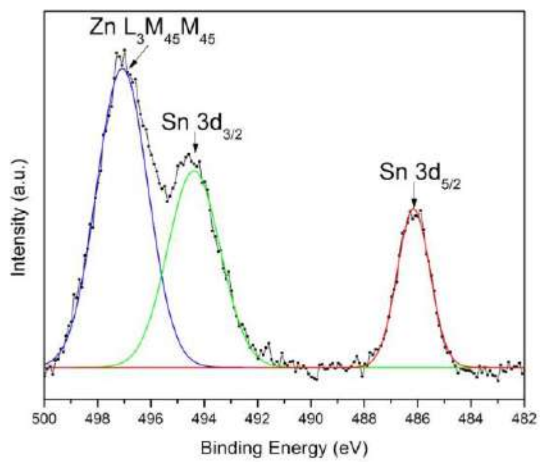

Figure 5. High-resolution XPS spectra of the Sn 3d core level and Auger peak the Zn $L_3M_{45}M_{45}$ of CZTS thin film.

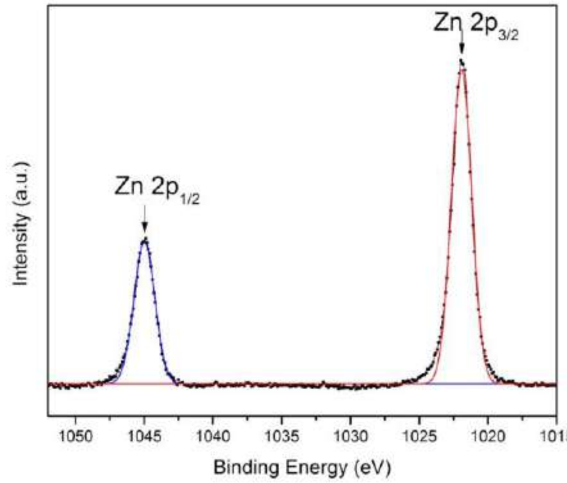

Figure 6. High-resolution XPS spectra of the Zn 2p core level of CZTS thin film.

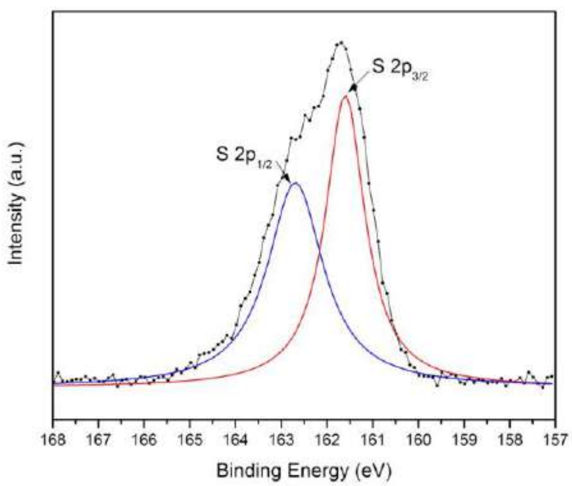

Figure 7. High-resolution XPS spectra of the S 2p core level of CZTS thin film.

4 CONCLUSIONS

EDAX 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 suggests non Sn_xS_y phase on the top of the surface, this results is according to the EDAX 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. The synthesis of CZTS semiconducting compound is not easy to achieved, however sequential metal precursor evaporation process in presence of sulfur when is performed the sequence Cu/Sn/Zn results in a single Kesterite phase with tetragonal structure according to XRD of CZTS thin films.

5 ACKNOWLEDGMENT

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