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XPS Depth Profile Study of Sprayed CZTS Thin Films

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Abstract. XPS depth profile studies were carried out to analyze the composition and stoichiometry of sprayed CZTS thin films giving an efficiency of 1.85% in CZTS based thin film solar cell. Surface layers were nearly stoichiometric (Cu:Zn:Sn:S=2:1:1:4) whereas the inner layers were found to be Copper rich in composition making it electrically more conductive.

Keywords: CZTS, X-ray photoelectron spectroscopy, Depth profiling
PACS: 07.85.Nc, 79.60.-i, 61.72.S-, 81.70.Jb, 81.15.Rs

INTRODUCTION

Cu_2ZnSnS_4 (CZTS) is a novel thin film material used as absorber in solar cells instead of CIS, CISe, CIGS and CIGSe thin films [1-2]. CZTS films contain neither toxic materials nor rare earth metals. In addition, the films can be easily prepared through non-vacuum processes like Spray Pyrolysis [3-5]. It is essential to have an idea of stoichiometry of surface and bulk of CZTS film as it has a profound impact on cell performance. In the present work, we investigated stoichiometry of CZTS thin films using X-ray photoelectron spectroscopy (XPS) depth profiling. This CZTS thin film was used as the absorber layer in thin film solar cell working with an efficiency of 1.85% [6].

EXPERIMENTAL

The studied CZTS thin films were prepared by automated Chemical Spray Pyrolysis (CSP) technique. More details about the synthesis can be found in [6]. Composition of the CZTS thin film was studied using XPS [Kratos Analytical AMICUS spectrometer fitted with the Mg Kα/Al Kα dual anode X-ray source]. Here Mg Kα (1253.6 eV) anode was used at 120W (12KV & 10mA). DuPont energy analyzer can be operated at three different pass energies (25eV, 75eV & 150eV) using electron transfer lens. Ultra high vacuum proved adhesive carbon tape with the size of about 5×5 mm^2 was used to mount the films on stainless steel sample holder of diameter 1 cm.

Binding energy (BE) of Ag $3d_{5/2}$ at 368.3 eV was used to calibrate the spectrometer. BE values of the samples were calculated on the basis of C 1s peak at 284.6 eV of ostentatious Carbon. Main core level photoemission spectra (with 25 meV energy increment) of C, Cu, Zn, Sn, S and O were recorded and relative atomic concentrations of the elements were determined from appropriate core level integrated peak areas and sensitivity factors provided by the Kratos analysis software Vision 2.2. Linear back ground subtraction is used for the calculations of relative atomic concentrations. High speed Ar^+ ion sputtering gun (2KV, 20mA, 10^{-3}Pa, and 15s/cycle) was used for the surface cleaning from atmospheric contaminants and for the bulk composition information.

RESULTS AND DISCUSSIONS

According to the XPS depth profiling spectra of CZTS thin films, the BE of Cu $2p_{3/2}$, Zn $2p_{3/2}$, Sn $3d_{5/2}$ and S $2p_{3/2}$ core levels after surface cleaning are located at 932.3 eV, 1023 eV, 485.3eV, 160.8eV respectively (Fig.1). Survey (wide) spectrum reveals no traces of any other material on the clean surface as well as in the bulk of the CZTS thin film. Carbon and Oxygen contaminations on the surface were reduced significantly after the first Ar^+ ion etching cycle. Carbon contamination is unavoidable in almost all the preparations while presence of Oxygen

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in the surface may be due to our deposition technique.

No chemical shift of were observed in Cu 2p, the Zn 2p, and the Sn 3d, the S 2p, during Ar+ ion sputtering. Also, no indications of “shake-up” satellite on the Cu 2p core level spectra were found (fig.1 (a)). Due to the overlapping of the S $2p_{3/2}$ level with the S $2p_{1/2}$ level, the S $2p_{3/2}$ core level binding energy was determined by the core level curve fitting procedures (fig.1 (d)).

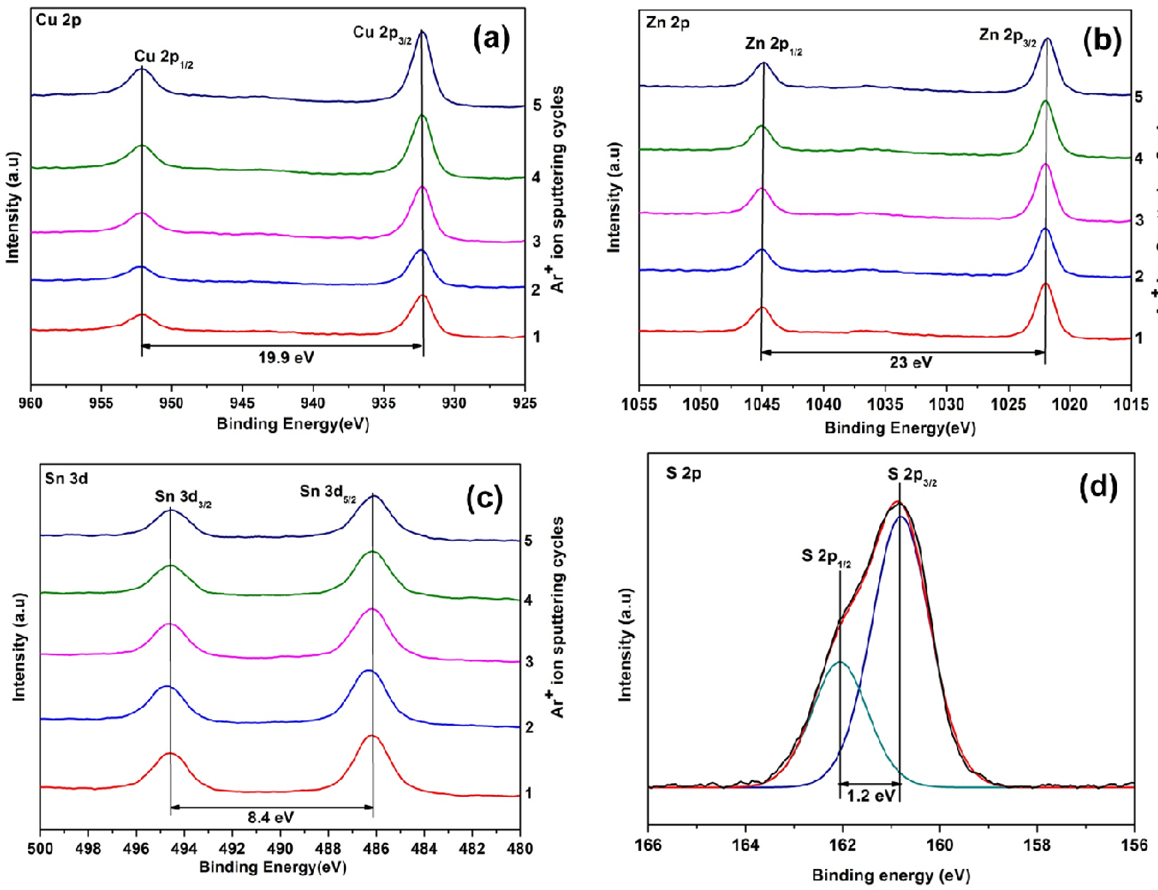

FIGURE 1. XPS core level peaks of CZTS thin film (a)Cu 2p (b)Zn 2p (c)Sn 3d after different Ar+ ion sputtering cycles and (d) S 2p core level curve fitting.

Cu 2p core levels are separated by 19.9 eV which indicates the formation of Cu(I), while Zn 2p and Sn 3d core levels show peak splitting of 23 eV and 8.4 eV respectively which confirms presence of Zn(II) and Sn(IV). Peak separation in BE was 1.2eV for S $2p_{3/2}$ and S $2p_{1/2}$ peaks, which were located at 161.1 and 162.3eV and were consistent with the expected range of 160–164eV for S in sulfide phases [7-8].

The relative atomic concentrations of Cu, Zn, Sn and S were determined by integrating the area under the core level peaks. The relative atomic concentrations of the elements vs. the Ar+ ion sputtering cycles of CZTS thin film is represented in Fig.2. It can be seen that surface composition of the film is different from the bulk composition.

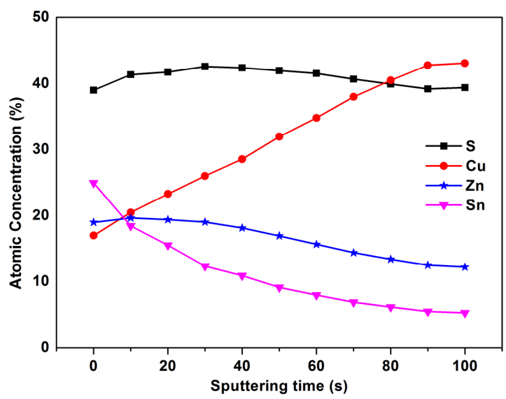

FIGURE 2. Depth profile of CZTS thin film

Compositional changes are characterized using different component ratios. We present three different compositional ratio profiles of CZTS thin films: (S)/(Zn+Cu+Sn), Cu/(Zn+Sn) and Zn/Sn in Fig.3.

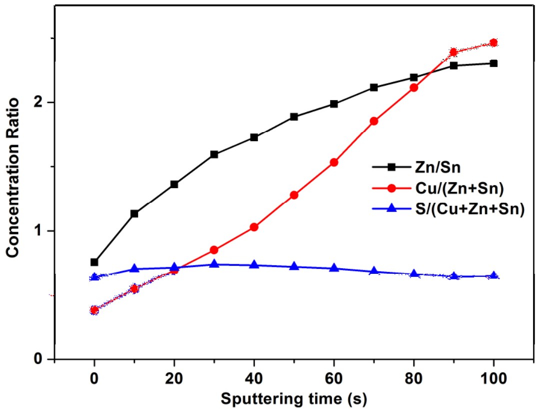

FIGURE 3. Elements concentration ratios with Ar+ ion sputtering time

The Zn/Sn ratio changes from 0.75 at the surface to 2.2 in the bulk. At the same time, the Cu/(Zn+Sn) ratio increases from 0.4 at the surface to 2.4 in the bulk. These metal component ratios indicate the copper deficiency on the thin film surface [9-10]. And finally, the (S)/(Zn+Cu+Sn) ratio remains almost constant in the range 0.6 to 0.75.

CONCLUSION

XPS analysis in this report reveals that composition of CZTS thin films close to the surface appears to have almost the stoichiometric compositional ratio of Cu:Zn:Sn:S=2:1:1:4 while that of the inner layers of the film shows excess Cu; This may be resulting in low resistivity of the film near to the electrode leading to higher photo current.

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