



XPS study of CZTSSe monograin powders

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ABSTRACT

The surface and bulk composition of $\text{Cu}_2\text{ZnSn}(\text{Se}_x\text{S}_{1-x})_4$ (CZTSSe) monograin powders were investigated by X-ray photoelectron spectroscopy (XPS). The concentration depth profiling of CZTSSe monograin powders was obtained by Ar^+ ion etching.

According to the XPS spectra of CZTSSe monograin powder, the binding energies of Zn $2p_{3/2}$, Cu $2p_{3/2}$, Sn $3d_{5/2}$, S $2p_{3/2}$ and Se $3d_{5/2}$ core levels after surface cleaning are located at 1021.6 eV, 932.4 eV, 486.1 eV, 161.5 eV, 53.9 eV, respectively. From XPS depth profile analysis, Cu deficiency and the excess of chalcogenides on the powder crystals surface were observed.

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1. Introduction

Quaternary compounds $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) solid solutions $\text{Cu}_2\text{ZnSn}(\text{Se}_x\text{S}_{1-x})_4$ (CZTSSe) have attracted increasing attention as possible absorber materials for thin film solar cells. Their elemental constituents are abundant on the Earth's crust and they have optimal properties such as *p*-type conductivity, optimal direct bandgap and high absorption coefficients ($> 10^4 \text{ cm}^{-1}$) for solar energy conversion [1,2]. Recently, in the beginning of 2010, the newest liquid-processed CZTSSe thin film solar cell efficiency reached 9.66% [3].

Cu depletion layers has been found on $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGSe) polycrystalline thin films with integral concentration ratio $([\text{Cu}]/[\text{In}] \pm [\text{Ga}]) =$ in the range of 0.82–0.9. Cu depletion in CIGS materials and its influence on the physics of related solar cells has been discussed for the past 15 years. The Cu depletion was explained by the surface reconstruction model [4–6]. When the In and Ga are substituted by Zn and Sn, the Cu–Se bonding characteristic remains similar to that of CuInSe_2 [7]. In order to find the occurrence of the similar Cu depletion phenomenon in CZTSSe materials, the depth-dependent compositional analysis by XPS was performed on a single-crystalline CZTSSe powder. This CZTSSe monograin material was used as the absorber in the monograin layer thin film solar cell working with 6% efficiency [8].

2. Experimental

The studied $\text{Cu}_2\text{ZnSn}(\text{Se}_x\text{S}_{1-x})_4$ single-crystalline powder material with the particles diameter of 50 μm (monograins) was synthesized from CuSe, CuS, ZnSe, ZnS, SnSe, and SnS precursors in molten

potassium iodide (KI) at 720 °C in sealed vacuum ampoules. More details about the synthesis can be found in Ref. [1]. The obtained materials consisted of single-crystalline particles with tetragonal shape and *p*-type conductivity. KI was removed by washing with deionised water. The phase structure and the chemical composition of the monograin powder crystals were analyzed by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX) measurements. The information on the composition of the elements in the CZTSSe monograin powder crystals surface were studied using X-ray photoelectron spectroscopy (XPS) in the Kratos Analytical AXIS ULTRA DLD spectrometer fitted with the monochromatic Al K_{α} X-rays source and the achromatic Mg K_{α} /Al K_{α} dual anode X-ray source. The monochromatic Al K_{α} anode (1486.6 eV) was used at 150 W and 15 kV. The 180° hemispherical energy analyser with 165 mm mean radius was operated at the pass energy of 40 eV using the hybrid lens mode. XPS spectra were recorded at 90° takeoff angle from the surface of the sample holder using the aperture slot of 300 × 700 μm . Ultra high vacuum proved adhesive carbon tape with the size of about 3 × 4 mm^2 was used to mount the CZTSSe monograin powder on stainless steel 130 × 15 mm^2 sample bars. Binding energy values were calculated on the basis of the C 1s peak at 284.6 eV. The main core level photoemission spectra (with 0.1 eV energy increment) of Zn, Cu, O, Sn, C, S, and Se were recorded. The relative atomic concentrations of zinc, copper, tin, and selenium were determined from the appropriate core level integrated peak areas and sensitivity factors provided by the Kratos original analysis software Vision 2.2.8. S 2p peak area was determined by core level curve fitting procedures due to overlapping with Se 3p core level. Shirley background subtraction was used for the calculations of relative atomic concentrations. Minibeam I ion (Ar^{\pm}) source (4 kV, 20 mA, 5×10^{-8} Torr, 30 s per cycle) was used for the surface cleaning from atmospheric contaminants and for the bulk composition information. Depth profile was acquired until the intensity of core level peaks reached to constant value.

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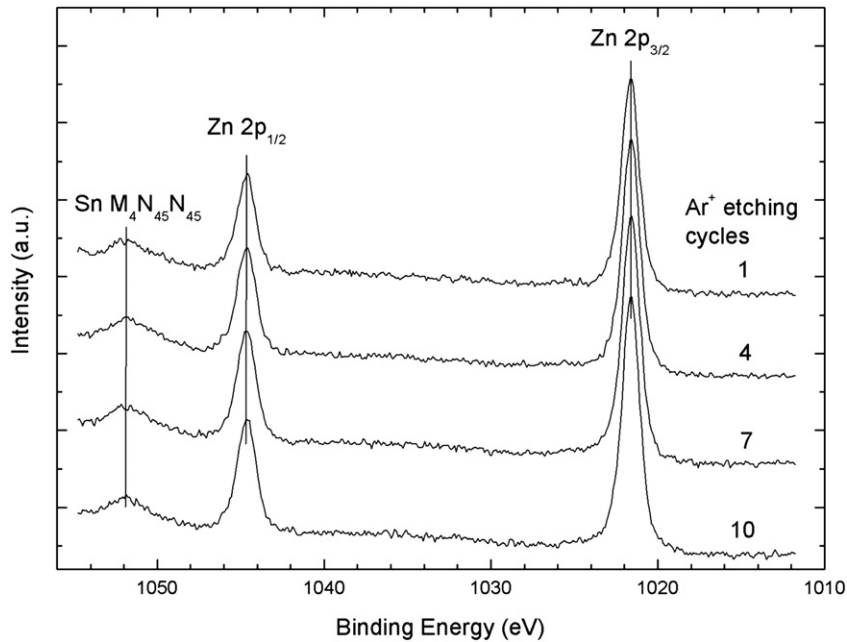


Fig. 1. High-resolution XPS spectra of the Zn 2p core level and the Auger peak Sn M₄N₄₅N₄₅ of a CZTSSe monograin powder clean surface and after different Ar⁺ ion sputtering cycles.

3. Results

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; Zn/Sn = 1.02 and (Se + S)/(Cu + Zn + Sn) = 1.05. According to the EDX quantitative analysis the molar ratio of the elements is: Cu:Zn:Sn:(S + Se) = 1.82:1.02:1.00:4.03. The kesterite phase of these CZTSSe monograin powder crystals was confirmed by XRD measurements.

According to the XPS spectra of CZTSSe monograin powder crystals, the binding energies (BE) of Zn 2p_{3/2}, Cu 2p_{3/2}, Sn 3d_{5/2}, S 2p_{3/2}, and Se 3d_{5/2} 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. The survey (wide) spectrum reveals no traces of any flux material on the clean surface and in the bulk of the CZTSSe monograin material. The amount of oxygen and carbon contamination on the surface reduces significantly already after the first Ar[±] ion etching cycle. Oxygen and carbon contamination is due to the sample storage in a plastic vessel at atmospheric conditions. The Sn M₄N₄₅N₄₅ Auger peak at BE = 1051.8 eV (kinetic energy KE = 434.9 eV) can be observed on

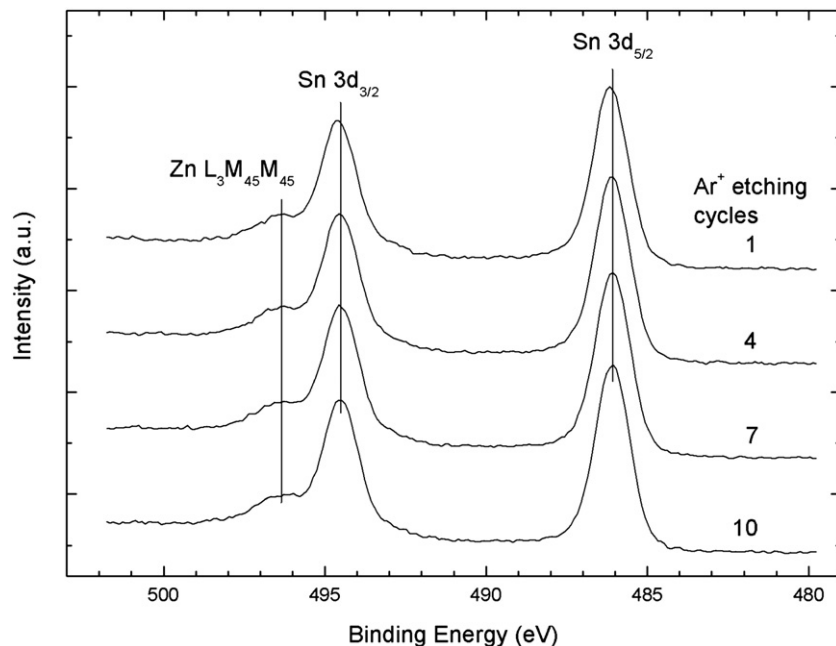


Fig. 2. High-resolution XPS spectra of the Sn 3d core level and Auger peak the Zn L₃M₄₅M₄₅ of a CZTSSe monograin powder clean surface and after different Ar⁺ ion sputtering cycles.

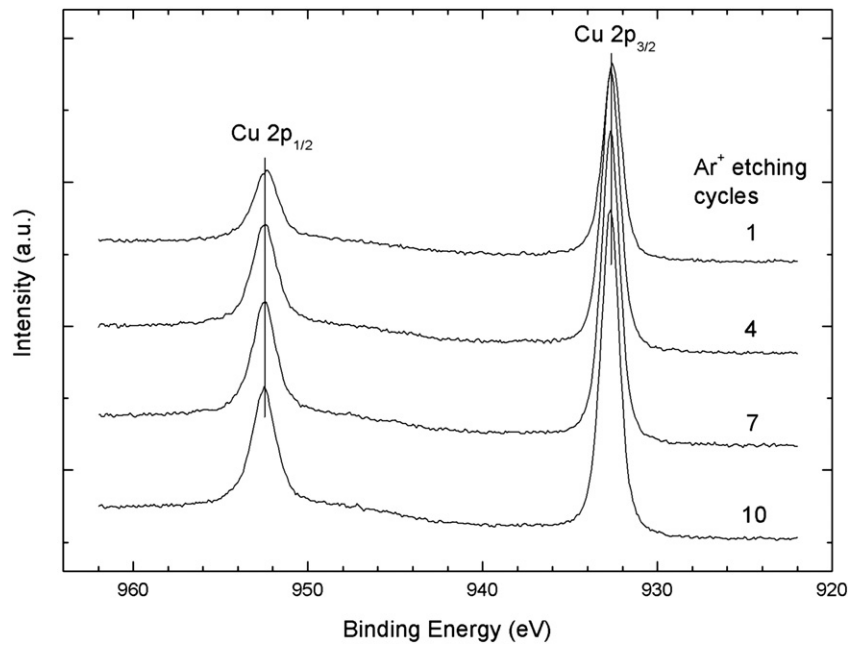


Fig. 3. High-resolution XPS spectra of the Cu 2p core level of a CZTSSe monograin powder clean surface and after different Ar⁺ ion sputtering cycles. No traces of “shake-up” satellites can be observed.

the high energy side of the Zn 2p core level spectra (Fig. 1). The Zn L₃M₄₅M₄₅ 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 (Fig. 2). No chemical shift of the Zn 2p, the Cu 2p, the Sn 3d, the S 2p, and the Se 3d core levels and the Sn M₄N₄₅N₄₅ and the Zn L₃M₄₅M₄₅ Auger peaks were observed during Ar⁺ ion sputtering. Also, no indications of “shake-up” satellite on the Cu 2p core level spectra were found (Fig. 3). The relative atomic concentrations of Zn, Cu, Sn and Se were determined from high-resolution XPS core level spectra integrated peak areas. Due to the overlapping of the S 2p core level with the Se 3p core level, the S 2p peak area was determined by the

core level curve fitting procedures. The high-resolution spectra of the S 2p and the Se 3p components are shown in Fig. 4.

The relative atomic concentrations of the elements vs. the Ar⁺ ion sputtering cycles of CZTSSe monograin powder are presented in Fig. 5. It can be seen that the surface composition of the monograins is different from the bulk composition. Compositional changes are characterised using different component ratios. Fig. 6 presents four different compositional ratio profiles of CZTSSe monograin powder surface: (S + Se)/(Zn + Cu + Sn), Cu/(Zn + Sn), Zn/Sn and S/(S + Se). From these results it can be seen that the concentration ratio between sulphur and selenium has the constant value of about 0.7. The zinc

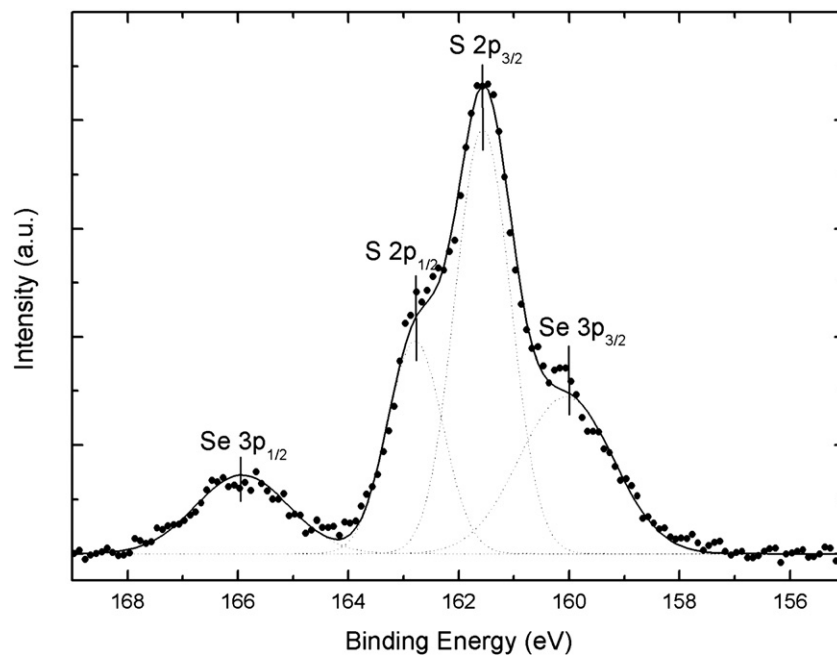


Fig. 4. High-resolution XPS spectra of the S 2p and the Se 3p core level curve fittings to evaluate the S 2p peak areas.

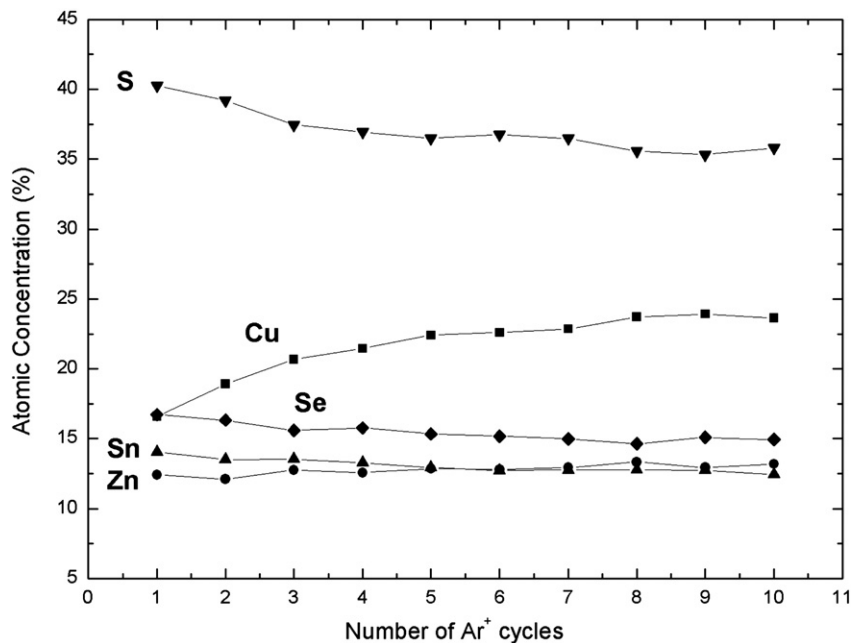


Fig. 5. The elemental concentrations depth profiling of a CZTSSe monograin powder crystals surface.

relation to tin changes from 0.88 at the surface to 1.06 in the bulk. At the same time, the $\text{Cu}/(\text{Zn} + \text{Sn})$ ratio increases from 0.63 at the surface to 0.92 in the bulk. These metal component ratios indicate the copper deficiency on the powder crystal surface. And finally, the $(\text{S} + \text{Se})/(\text{Zn} + \text{Cu} + \text{Sn})$ ratio decreases from 1.32 to 1.03 revealing that similar to CIGSe materials, Cu depletion may occur in CZTSSe crystals surface. Also, CZTSSe crystals can be covered by some extra sulphur and selenium containing phases. As the full width at half maximum (FWHM) of Sn 3d core level is wider than Zn 2p and Cu 2p core level peaks FWHM, most probable secondary phases on the powder crystals surfaces are tin sulfides and tin selenides. Minor traces of additional

phases were also found by Raman spectroscopy [9]. According to these XPS results the component ratios close to the bulk corresponds to the atomic ratio of the elements $\text{Cu}:\text{Zn}:\text{Sn}:(\text{S} + \text{Se}) = 1.90:1.06:1.00:4.07$, which is in good agreement with the EDX analysis.

4. Conclusions

The XPS analysis in this report reveals that the composition of CZTSSe monograin powder crystals close to the bulk appears to have almost the stoichiometric compositional ratio of $\text{Cu}:\text{Zn}:\text{Sn}:(\text{S} + \text{Se}) = 2:1:1:4$. This result was also confirmed by an independent EDX analysis.

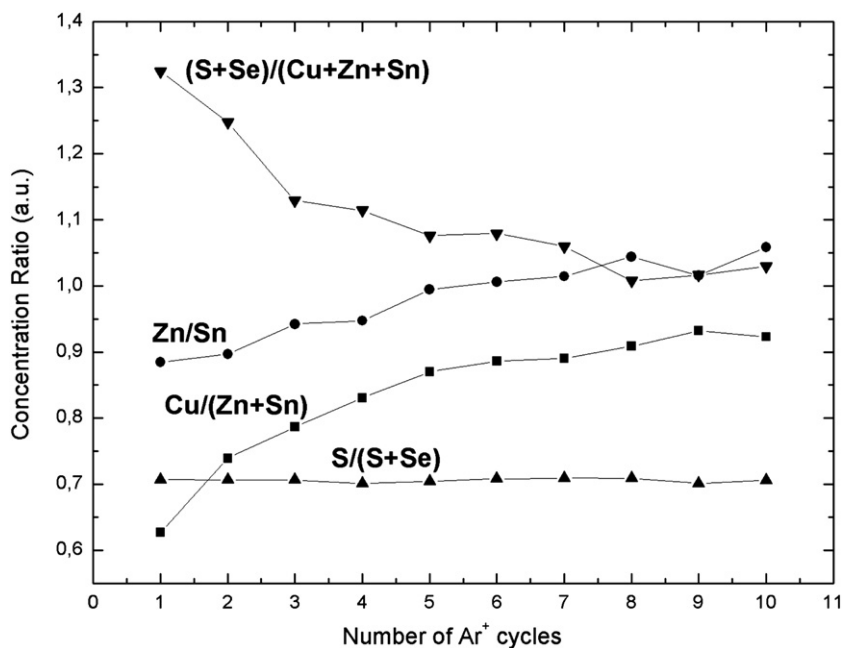


Fig. 6. Elements concentration ratios depending on the Ar⁺ ion etching times of CZTSSe monograin powder material surface.

No traces of the flux material (KI) were detected on the clean surface and in the bulk of crystals. The composition of the top surface layer of the CZTSSe monograin powder crystals shows the Cu deficiency and presumably has some extra sulphur and selenium containing phases directly on the surface. The determination of the accurate surface phase composition needs further investigations.

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