The Influence of Removal of Secondary Phases and Dissolution By-Product from the Surface of Cu₂ZnSnS₄ Film on the Photoelectrochemical Response of This Film

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The influence of surface treatment of as-synthesized Cu2ZnSnS4 (CZTS) thin films on the photocurrent response in the photoelectrochemical cell with Eu3+ contact has been studied. With our work we are the first, to our knowledge, to show that in order to achieve the maximal photocurrent response of CZTS, dissolution of copper sulfide in a KCN solution and subsequent dissolution of ZnS in a HCl solution is insufficient. An additional treatment in a KCN solution for only 10 s can results in the highest photocurrent density. XPS, photoelectrochemical and the Mott-Schottky measurements reveal a negatively charged layer of surficial chlorides on the CZTS film. This layer was captured during removal of the ZnS secondary phase from the CZTS film surface in a HCl solution. It has been shown that this layer is the reason why it was impossible to reach the maximum photocurrent. XRD, SEM and XPS measurements demonstrated the dissolution of copper sulfide in a KCN solution, zinc sulfide in a HCl solution and removal of a thin layer of copper chloride during a short (10 s) additional treatment in a KCN solution.

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One of the most promising candidates for the direct conversion of solar energy into electricity is the Earth-rich, inexpensive and nontoxic kesterite, copper zinc tin sulphide—Cu2ZnSnS4 (CZTS). CZTS is a p-type semiconductor with a carrier concentration of 1015–1018 cm−3, a direct band gap of about 1.5 eV and the light absorption coefficient above 104 cm−1. Most commonly, CZTS is fabricated employing a two-stage approach, where deposition of a metallic Cu, Zn and Sn (CZT) precursor layer on the Mo substrate is followed by sulphurization. Many different deposition methods of CZT, such as electrochemical deposition, spray pyrolysis, sputtering or thermal evaporation, have been employed for the deposition of metallic CZT layers. Amongst all these methods, the electrochemical deposition method (EDM) seems to offer the most convenient, simple and cost-efficient process for the deposition of a metallic CZT layer on the Mo substrate. In addition, EDM can potentially enable precise control of the CZTS film composition.

The CZTS absorber is the most critical part of the solar cell, because major processes required for a good conversion of solar energy to electricity occur precisely here. However, as a result of formation of various binary and ternary secondary phases such as Cu2SnS3, Cu2S–SnS, SnS2 and ZnS during the sulphurization process, the absorber layer unsuitable (unless additional treatment is applied) for fabrication of the solar cell. After CZT sulphurization, the kesterite surface composition can only be changed by surface treatment process, namely, by the removal of the secondary phases formed. Various properties of the CZTS absorber, including compositional, optical, electrical, and photovoltaic strongly depend on the success of the removal of the secondary phases from the kesterite surface. Research shows that etching of Cu2–xS with a KCN solution and ZnS with a HCl solution is an efficient way to remove secondary phases from the surface of CZTS. In the present study we formed a thin CZTS film on Mo foil. The mentioned film was formed by co-electrodeposition of a Cu—Sn layer, and subsequent electrodeposition of Zn layer, followed by the sulphurization process. The composition of CZT was Cu poor and Zn rich. This was done hypothesizing that only Cu2S and ZnS would be present on the surface of the CZTS after sulphurization. The composition of electrochemically deposited CZT was performed so, that after sulphurization and removal of secondary phases (Cu2S and ZnS) from the CZTS surface the final kesterite film was Zn rich (Zn/Sn = 1.18). According to reference, optimal photovoltaic properties of CZTS were obtained when the Zn/Sn ratio was in the range 1.1–1.3.

This study, to our knowledge, is the first showing several important aspects of the CZTS surface treatment process and its influence on the photocurrent response (PCR) (the photocurrent measurement in the photoelectrochemical cell (PEC) was selected for the evaluation of CZTS PCR). We demonstrate: (I) that after sulphurization and removal of secondary phases (Cu2S and ZnS) from CZTS surface the final kesterite film was Zn rich (Zn/Sn = 1.18). According to reference, optimal photovoltaic properties of CZTS were obtained when the Zn/Sn ratio was in the range 1.1–1.3.

Experimental

A Cu-Sn/Zn precursor layer was electrochemically deposited onto Mo foil (thickness 1.0 mm, purchased from Goodfellow). Prior to the electodeposition the Mo surface was mechanically polished using the Tegramin-25 (Stuers, Denmark) polishing system. Later Mo was ultrasonically washed in ethanol for 30 min, rinsed in a distilled water, immersed into a 20% NH4OH solution for 30 min and rinsed in distilled water. A detailed description of the electrochemical co-deposition of Cu–Sn alloy is presented elsewhere. Zn was galvanostatically coated in a stirred sulphate electrolyte solution: 2 M ZnSO4 + 1 M HSO4 (Sigma-Aldrich), (pH 4.1). A Cu–Sn layer of the desired composition (Cu/Sn = 65/35 at%) was obtained at the cathodic potential E C = −0.275 V vs Hg/HgSO4 reference electrode when passing a constant charge of 1.1 C. The Zn layer was deposited on the Cu–Sn layer using a current density of 30 mA cm−2 (0.45 C).

After the electodeposition the Cu–Sn/Zn precursor was soft annealed at a temperature of 300 °C for 60 min in a gas mixture of...
At 90% + H2 10%. The Cu-Sn–Zn precursor was sulfharized in a graphite container with 150 mg of sulphur powder at a temperature of 580 °C for 10 min. The temperature was increased at a rate of 20 °C min⁻¹.

Photoelectrochemical, spectroelectrochemical measurements were performed in a three-electrode electrochemical cell equipped with a quartz window. All these measurements were performed using ten typical CZTS samples. Chemical compositions of these samples are presented in Table I. The scattering of data, for example, photocurrent measurements, was approximately 6%. The results, presented in the Results and Discussion section of this manuscript, are measurements of one out of ten CZTS samples. An advanced electrochemical system Parstat 2273 from Princeton Applied Research (USA) was employed for all measurements. Mott-Schottky analysis was performed with a sinusoidal voltage perturbation with an amplitude of 0.005 V at a frequency of 1 kHz in a 0.1 M Eu(NO3)3 (Acros organics), aqueous solution (pH 2.4). The photoelectrochemical measurements of CZTS thin film electrodes were conducted with respect to the Hg/HgSO4 electrode and converted to the standard hydrogen scale (vs SHE). During photoelectrochemical measurements the CZTS thin film surface was illuminated with 505 nm LED Lumiled LXHLL—LE3C. The light intensity at the CZTS film electrode surface was about 100 mW cm⁻² as measured with a VLP-2000 power meter. The area of CZTS thin film exposed to the solution was 0.5 cm². A platinum wire was used as a counter electrode in photoelectrochemical measurements. A solution of 0.1 M Eu(NO3)3 (Acros organics), (pH 2.4) was used in photoelectrochemical investigations. Solutions were prepared using analytical grade Eu(NO3)3 and triply distilled water. The electrolyte solution was purged with argon prior to the measurements.

All measurements were carried out at room temperature and under normal pressure. All samples before photoelectrochemical, spectroelectrochemical measurements were etched for 60 s in a 5% KCN (Sigma-Aldrich) aqueous solution and 180 s in 5% HCl at T = 75 °C. After that for 10 s in 5% KCN to remove a layer of surficial chlorides. All samples after each treatment in KCN and in HCl were rinsed in distilled water and dried with argon.

XPS measurements were carried out to obtain information on the elemental chemical states and surface composition of CZTS samples employing an upgraded Vacuum Generator (VG) ESCALAB MKII spectrometer fitted with a new XRX twin anode. The —non—monochromatized AlKα, X-ray source (hα = 1486.6 eV) was operated at the power of 300 W (20 mA/15 kV) and the pressure in the analysis chamber was lower than 5 × 10⁻⁸ Pa during spectrum acquisition. The spectra were acquired employing an electron analyzer with the pass energy of 20 eV for narrow scans and resolution of 0.05 eV or with the pass energy of 100 eV for survey spectra. All spectra were recorded at a 90° take-off angle and calibrated from the hydrocarbon contamination using the C 1 s peak at 284.8 eV. Spectra calibration, processing and fitting routines were done using Advantage software (5.962) by Thermo VG Scientific. Core level peaks of Cu 2p, Zn 2p, Sn 3d, Cl 2p, S 2p, C 1s and O 1s were analyzed using a nonlinear Shirley-type background and the calculation of the elemental composition was performed on the basis of Scafield’s relative sensitivity factors. The accuracy of the binding energy evolution was ±0.1 eV. The sensitivity of the method used was 0.1 at%. Some samples were etched at a current density of 50 μA cm⁻² in the UHV preparation chamber at the pressure of ~5 × 10⁻¹⁰ Pa using a 3 kV Ar⁺ beam energy at the angle of ~60°.

The XRD studies were conducted using an X-ray diffractometer Smart Lab (Rigaku) with a 9 kV rotating Cu anode X-ray tube. The primary X-ray beam was conditioned by a multilayer Ni/graphite monochromator CBO (cross beam optics) in the case of grazing incidence (GI) XRD measurements.

The SEM characterization of CZTS films surface morphology and EDX analysis of the precursors and films were carried out in a dual beam system FE-SEM-FIB Helios Nanolab 650 (FEI Company) equipped with an X-ray spectrometer X-Max (Oxford Instruments).

**Results and Discussion**

The chemical composition is a very important factor for attainment of the highest photocurrent values, particularly the Cu/(Zn + Sn) and Zn/Sn ratios. The chemical compositions of the CZT precursor and CTZS film measured by EDX after each chemical treatment of the surface of CZTS sample are presented in Table I.

The values in Table I were obtained from measurements of ten typical CZTS film samples prepared as described in the Experimental part of this work. The chemical composition of CTZS film (Zn/Sn = 1.18 and Cu/(Zn + Sn) = 0.87) was determined after the final surface treatment. These ratios are within the ranges of the optimal ratios (Zn/Sn = 1.1–1.3 and Cu/(Zn + Sn) = 0.8–0.9).

According to Refs. 6, 12, 23–25 these optimal ratios are best suited for the further fabrication of a highly efficient CZTS solar cell.

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**The as-grown CZTS sample.**—After soft annealing the CZT precursor was quite highly enriched with zinc (Zn/Sn = 1.35), but depleted in copper (Cu/(Zn + Sn) = 0.9) (see Table I). After the sulfurization the Zn/Sn ratio significantly decreased (Zn/Sn = 1.03) (see Table I), while that of Cu/(Zn + Sn) increased (Cu/(Zn + Sn) = 1.14) (see Table I), which means that part of the zinc was lost during the sulfurization procedure.

Figure 1 depicts XRD patterns of CZTS film on the Mo foil substrate. The lower pattern is for the as-grown CZTS film and it shows CuS (# 00-002-1284) peaks along with those of kesterite, i.e. Cu2ZnSnS4 (# 04-018-9747).

Figure 2 shows top view SEM images of the CZTS film immediately after the formation (image a) and after the immersion into a KCN solution (image b) and subsequently into a HCl solution (image c). On image (a) one can see large crystals which represent CuS according to the data of EDX analysis.

To identify the chemical composition of CZTS films surfaces apart survey spectrum (not presented in this manuscript) a high resolution XPS spectrum was recorded for Cu 2p, Zn 2p, Sn 3d, S 2p regions. Note that low intensity Cu 1s and O 1s peaks as contamination are present on all the as-grown and treated surfaces causing attenuation of the signals from underlying kesterite atoms. The Sn 3d5/2 and Sn 3d3/2 peaks are present at 495.4 eV, respectively, with a separation of 8.1 eV, for all samples, which indicates the Sn (IV) state (not presented in this manuscript).

The as-grown and with additional treatment in KCN and HCl solutions these CZTS films are shown in Figs. 3a–3d. The binding energies of S 2p,

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**Table I. Composition (at%) and elements ratio in CZT and CZTS films.**

| Sample                  | Cu%         | Zn%         | Sn%          | S%          | Zn/Sn | Cu/(Zn + Sn) |
|-------------------------|-------------|-------------|--------------|-------------|-------|--------------|
| CZT soft annealed        | 47.7 ± 0.8  | 30.26 ± 0.9 | 22.34 ± 0.7  | —           | 1.35  | 0.9          |
| CZTS                    | 25.73 ± 0.9 | 11.49 ± 0.8 | 11.17 ± 0.4  | 51.61 ± 1.4 | 1.03  | 1.14         |
| CTZS + KCN              | 21.11 ± 0.7 | 14.53 ± 0.6 | 11.29 ± 0.5  | 53.07 ± 1.1 | 1.29  | 0.82         |
| CTZS + KCN + HCl        | 21.61 ± 0.6 | 13.18 ± 0.7 | 11.26 ± 0.6  | 53.95 ± 1.2 | 1.17  | 0.88         |
| CTZS + KCN + HCl + KCN  | 21.35 ± 0.5 | 13.22 ± 0.6 | 11.20 ± 0.3  | 54.23 ± 1.0 | 1.18  | 0.87         |

a) After additional etching in a 5% KCN solution for 10 s.
Cu2p3 and Zn2p3 were determined by curve fitting of the experimental data after the Shirly background subtraction in order to follow the evolution of these three elements.

As expected, XPS measurements (see Fig. 3a) show that on the kesterite surface (immediately after sulphurization and without any chemical treatment) one can find secondary phases of Cu2S and ZnS poor in Cu and in Zn as compared to the nominal Cu:Zn:Sn:S—2:1:1:4 stoichiometry (the composition based on EDX measurements of the CZTS film is presented in Table I).

On the surface of the as-grown film (Fig. 3a) we observe S2p spectrum at binding energies of 161.3 eV and 162.4 eV with the peak splitting of 1.1 eV, related mainly to the sulfide S\(^{2-}\) state as Cu\(_2\)S or ZnS.\(^{30}\) The Cu2p3 spectrum after the fitting procedure shows three peaks with the main one of CZTS (at 931.9 eV) and Cu\(_2\)S (at 932.3 eV). Zn2p3 was also deconvoluted into four peaks ascribed to kesterite, ZnS (at 1021.6 eV), ZnO (at 1022.2 eV) and a minor amount of ZnSO\(_4\) (at 1023.1 eV).

The photocurrent measured in PEC was chosen in this work as a method to characterize the quality of our CZTS samples before and after each surface treatment. The study presented in our manuscript is associated with measurements of the photocurrent in a photoelectrochemical cell with an Eu\(^{3+}\) contact. Measurements of this type is a quick, convenient, and reliable way to evaluate the photoelectric activity of layers of a kesterite absorber and predict its suitability for the subsequent formation of solar cells.\(^{2,27,28}\) An alternative assessment method requires the complete fabrication of a solar cell, and only then is it possible to measure its photovoltaic activity. As a result, this method is much more expensive and labour intensive as compared to measuring the photocurrent response of a CZTS absorber in a PEC cell. In a number of research works\(^{2,27,28,31}\) the above described approach for evaluation of the quality of CIGS and CZTS adsorbers was used. It was shown\(^{31}\) that the absorber exhibiting the largest photocurrent measured in PEC, provides the best photovoltaic characteristics of the solar cell based on it. The photocurrent response (see Fig. 4) was recorded under the linear potential sweep at the cathodic potential of 0.005 V s\(^{-1}\) and under chopped (2 s light on and 2 s light off) 505 nm LED light (100 mW cm\(^{-2}\)) illumination of the CZTS film surface. A relatively short (2 s) cathodic photocurrent pulse increased every time when the electrode potential became more negative (see Fig. 4). The increasing cathodic electrode potential resulted in increased band bending (at the semiconductor/electrolyte interface) in the semiconductor. The latter processes contributed to the increase in photocurrent, as an increasing number of photogenerated electrons took part in the reduction reaction, see Eq. 1 at the semiconductor/electrolyte interface. Figure 4 illustrates the differences in cathodic photocurrent under chopped 505 nm illumination of the same CZTS film before and after each CZTS surface treatment.

\[\text{Eu}^{3+}(aq) + e^- + h\nu \rightarrow \text{Eu}^{2+}(aq) \]  

Our CZTS film, immediately after formation and without any chemical treatment shows a very small photocurrent (Fig. 4, plot (a)). This is not surprising, since the secondary phase Cu\(_2\)S overlying the surface of our kesterite sample, blocks reduction reaction (1) on it. Another explanation for such a small photocurrent could be also that the Cu\(_2\)S crystals act as traps for electrons and holes and enhance recombination.\(^{23}\)

**The as-grown CZTS sample + treated in KCN.**—The same CZTS film sample after photocurrent measurements in PEC (see
Fig. 4, plot (a) was treated with a KCN solution to remove the secondary phase Cu$_2$S from the film surface. The CZTS treatment in a KCN solution resulted in inverse changes of the ratios, i.e., CZTS regained its Zn rich and Cu poor composition and that was a result of copper sulfide dissolution (the ratios: Zn/Sn = 1.29, Cu/(Zn + Sn) = 0.82 (see Table I)). The conclusion was supported by the data of XRD measurements of both the as-synthesized CZTS film and the same film after KCN treatment (Fig. 1). The upper XRD pattern in Fig. 1 depicts the same film after its immersion in KCN. The absence of XRD peaks of Cu$_2$S phase proves that Cu$_2$S has been dissolved in
that of the as-grown one, concerning the photocurrent of the as-grown CZTS sample. Plot (a)—the photocurrent of the as-grown CZTS sample; plot (b)—the photocurrent of the as-grown CZTS sample + 60 s in KCN; plot (c)—the photocurrent of the as-grown CZTS sample + 60 s in KCN + 180 s in HCl; plot (d)—the photocurrent of the as-grown CZTS sample + 60 s in KCN + 180 s in HCl + additional 10 s in KCN. The insert shows two last cathodic photocurrent impulses taken from Fig. 4 plot (d).

After the immersion into a KCN solution in Fig. 2 (image b) those large Cu2S crystals (see image a) are not seen on the surface of the CZTS film. At the same time a lot of small white grains become visible on the surface of CZTS (image b). The presence of these white grains was confirmed by EDX analysis. The S2p spectrum exhibits two binding energies at 161.5 eV in pure ZnSO4. The insert shows the EDX analysis of these white grains indicating that these white grains were ZnS.

According to XPS measurements, Fig. 3b clarifies the chemical nature of the surface of the CZTS film after its immersion in KCN. The S2p spectrum exhibits two binding energies at 161.5 eV in pure ZnS and 162.7 eV in pure CZTS. Sample etching in KCN reveals distinctions in the XPS spectra of Cu2p3 and Zn2p3 with respect to that of the as-grown one, confirming the dissolution of CuS and ZnSO4.

The same CZTS film after the removal of Cu2S from the surface, shows the chopped cathodic photocurrent (the cathodic photocurrent is the evidence that the tested CZTS film is a p-type semiconductor).

These photocurrent measurements in PEC are shown in Fig. 4, plot (b). The photo current response reached $i_{ph} = 1.15 \text{ mA cm}^{-2}$ at $-0.324 \text{ V vs SHE}$ polarization under 100 mW cm$^{-2}$ of wavelength 505 nm illumination. This finding confirms that the CuS phase was completely removed from the CZTS sample surface. As a result, we have produced a CZTS surface on which photoelectrochemical reaction 1 at the interface of CZTS surface and electrolyte may readily occur. Under illumination of chopped 505 nm LED light (100 mW cm$^{-2}$) (the light energy is higher than the band gap $E_{gap} \approx 1.5 \text{ eV}$) of the CZTS film) electrons were moved from the valence band to the conduction band. From there they were driven to the solid/electrolyte interface and finally took part in the reduction of Eu$^{3+}$ ions (Eq. 1), creating the cathodic photocurrent response.

The as-grown CZTS sample + treated in KCN + treated in HCl—The same CZTS film sample after photocurrent measurements in PEC (see Fig. 4, plot (b)) was treated in a HCl solution to remove the ZnS secondary phase from the CZTS surface. Figure 2, image (c) depicts the surface of the CZTS film after immersion into a HCl solution, the absence of white grains proves that ZnS has been dissolved. The EDX measurements confirm this result (see Table I). The ratio Zn/Sn decreases (Zn/Sn = 1.17), while the ratio Cu/(Zn + Sn) increases (Cu/(Zn + Sn) = 0.88), which is the result of the dissolution of zinc sulfide.

The XPS spectra in Fig. 3(c) directly show changes in the same CZTS films after immersion in HCl and selective removal of the top ZnS layer with no affect on the main CZTS phase. This agrees with strong selectivity of this etchant. Small amounts of ZnO (at 1022.1 eV) and CuCl (at 932.4 eV) were also detected after etching with HCl.

The results of etching in HCl suggest two most likely premises why, after the removal of the ZnS phase from the surface of the CZTS film, the expected photocurrent must be larger than the photocurrent (see Fig. 4, plot (b)) after etching in KCN. The first premise—the ZnS phase, prior to its removal from the sample surface, blocks the active region of the surface where the reaction (see Eq. 1) could occur. The second premise—the chemical composition (Zn/Sn = 1.17 and Cu/(Zn + Sn) = 0.88, see Table I) of the CZTS film is within the ranges of the optimal ratios (Zn/Sn = 1.1–1.3 and Cu/(Zn + Sn) = 0.8–0.9 in accordance with references 6,12,23–25), which is suitable for further fabrication of a highly efficient CZTS solar cell.

Therefore, after removal of the ZnS phase, the photocurrent should be large (at the same illumination of 100 mW cm$^{-2}$) as compared to the photocurrent in Fig. 4, plot (b). Figure 4, plot (c) depicts the photocurrent measured in PEC after removal of ZnS from the CZTS film surface. One can recognize, that the value of the photocurrent in comparison with that of the photocurrent in Fig. 4, plot (b) is significantly lower at the same cathodic polarization. The difference between the cathodic photocurrent onset in plot (b) Fig. 4 and in plot (c) Fig. 4, suggest that the working electrode of the CZTS film is polarized negatively (by $\Delta E_\text{pol} = 0.16 \text{ V}$) (see Fig. 4) after removal of the ZnS secondary phase. This polarization of the working electrode, after removal of ZnS in a HCl solution can occur due to the formation of a negatively charged surficial layer. The data of XPS measurements (Fig. 3c), suggest that after immersion of the CZTS film in HCl solution, only CZTS and CuCl were formed on the sample surface. Further XPS measurements revealed that after the etching of this sample by Ar+ ions for 30 s (a layer of about 5 nm thick was removed) only CZTS was detected on the sample surface. This means that chlorides adsorbed by the CZTS surface formed a CuCl surficial layer of about 5 nm in thickness. This negatively charged surficial layer should lead to changes in the capacity of the double layer and in the potential drop across the Helmholtz layer. We could define these changes by the Mott-Schottky measurements.

Figure 5 reveals the Mott-Schottky measurements of the same CZTS sample. Plot (a) after immersion in KCN. Plot (b) after immersion in KCN + immersion in HCl. Plot (c) after immersion in KCN + immersion in HCl + an additional immersion in KCN solution for 10 s. The plots in Fig. 5 reveal the changes in flat band

![Figure 4. Photocurrent measurements in PEC illustrate the differences in cathodic photo current under chopped 505 nm illumination of the same CZTS film before and after each CZTS surface treatment.](image)

![Figure 5. Mott-Schottky plots for the same Cu$_2$ZnSnS$_4$ thin film: plot (a) after immersion in KCN for 60 s; plot (b) after immersion in KCN for 60 s + immersion in HCl for 180 s; plot (c) after immersion in KCN for 60 s + immersion in HCl for 180 s + an additional immersion in KCN for 10 s. The Mott-Schottky measurements were performed in the darkness.](image)
potential after each CZTS film treatment (the three flat band potential values of a thin film were calculated: plot (a) $E_{FB}^a = E^b + kT/e = 0.346$ V; plot (b), $E_{FB}^b = 0.206$ V; and plot (c) $E_{FB}^c = 0.376$ V). This flat band potential shift is a good indication of formation of a layer of surficial chlorides on the CZTS film which occurs during its treatment in HCl (Fig. 5, plot (b)). The removal of this layer with the use of an additional treatment in KCl for ten seconds (Fig. 5, plot (c)) results, in flat band potential recovery almost to its initial value (Fig. 5, plot (a)).

The formation of the layer of surficial chlorides on the CZTS film leads to changes in the surface charging, which in its turn leads to changes in potential drop across the Helmholtz layer, negative electrode almost to its initial value (Fig. 5, plot (a)).

It is possible to evaluate the flat band potential of a p-type semiconductor by the following equation:33

$$\frac{1}{C^2} = \frac{2}{\varepsilon_0 \varepsilon N_{a} A} \left( E + E_{FB} \right) - \frac{kT}{e}$$

[2]

where $\varepsilon_0$ is the permittivity of vacuum ($8.854 \times 10^{-12}$ F m$^{-1}$), $\varepsilon$ is the dielectric constant of CZTS ($\varepsilon = 6.7$ was chosen for the calculations), $N_a$ is the acceptor density, which is calculated from the slope of the curve, $T$ is the operation temperature (298 K) and $k$ is Boltzmann’s constant ($1.38 \times 10^{-23}$ J K$^{-1}$). $E$ is the electron charge, $E_{FB}$ is the flat band potential, and $C$ is the depletion layer capacitance. According to Eq. 2 the carrier density of CZTS, which was additionally treated by fitting curves (Fig. 5, plot (c)), was $N_a = 2.6 \times 10^{17}$ cm$^{-3}$. The flat band potential of the thin film was evaluated by extrapolating the linear part of the Mott–Schottky plot to $1/C^2 = 0$ and equal to: $E_{FB} = E + kT/e = 0.376$ V vs SHE.

**Conclusions**

The photoelectrochemical, XRD, XPS, SEM, EDX and Mott-Schottky measurements showed that during the removal of the ZnS secondary phase from the CZTS surface in a HCl solution some amount of chlorides was captured by the Cu$_2$ZnSnS$_4$ surface resulting in formation of a thin negatively charged surficial layer. We were able to show that this local, thin layer drastically reduced the photocurrent response and negatively polarized the Cu$_2$ZnSnS$_4$ working electrode (by $\Delta E \approx -0.16$ V).

Thus, based on our results, we argue that additional treatment of only 10 s (to remove a layer of surficial chlorides from the CZTS film) in a KCl solution is needed for successful preparation of the CZTS film surface for further formation of the solar cell. The CZTS film after treatment in the order described elsewhere (and above in our paper) provides better photoelectrical properties for solar cell formation: a p-type conductivity, a carrier concentration $N_a = 2.6 \times 10^{17}$ cm$^{-3}$, the flat band potential $E_{FB} = 0.376$ V vs SHE) and a photocurrent density of 1.6 mA cm$^{-2}$ at the cathodic potential of $-0.324$ V vs (SHE) under 100 mW cm$^{-2}$ 505 nm illumination.

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