Current-voltage and capacitance study of light-induced metastabilities in CuZnSnS₄ thin film solar cells.

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Abstract

White, red and blue light-induced metastabilities in Cu₂ZnSnS₄(Se₄) solar cells were investigated by temperature dependent current-voltage measurements, drive level capacitance profiling, impedance and thermal admittance spectroscopy. A set of devices were studied where white and blue light soaking at room temperature led to degradation of the device performance, while after red light soaking the solar cell efficiency did not change.

We observed a significant effect of light soaking on capacitance data measured in both low and high-temperature ranges for these devices. In particular, the net doping concentration extracted from drive-level capacitance profiling substantially increased after light soaking treatments.

Low and high-temperature capacitance steps observed in the reference capacitance-frequency spectra were assigned to Fermi level pinning and bulk defects, correspondingly. Light soaking with different-wavelength light led to a shift of both steps toward the high-frequency range, and hence a decrease in the thermal admittance activation energies.

A low-frequency “inductive” loop was detected in the impedance spectra after light soaking, regardless of wavelength. It was proposed that the appearance of the “inductive” loop is due to the formation of a negative electric field at the highly defected CdS/Cu₂ZnSnS₄(Se₄) hetero-interface. This result also leads us to conclude that such electric field is responsible for the metastable behaviour of these devices at room temperature, while the low temperature metastable changes might have a different origin.

We also discuss the methodology for electrical characterization of the metastable solar cells in detail.

Keywords: kesterite solar cells, metastability, electrical characterization, impedance spectroscopy.

1. Introduction

The record performance for Cu₂ZnSnS₄(Se₄) (CZTSSe) thin film solar cells stands at 12.6% [1]. Also, several groups worldwide have overcome 9% [2–6] efficiency of CZTSSe

devices by using different approaches for the fabrication of the absorber layer and device architectures. This was accomplished through an understanding of the chemistry of secondary phases formation [7–10], material structural and optical properties [10–12] and optimization of the front- and

back contact interfaces [13,14]. However the record efficiency for CZTSSe thin film solar cells is still much lower than the theoretically estimated maximum, that is, about 30% [15]. It is believed that the efficiency limitation in CZTSSe solar cells is due to unfavorable structural defects acting as charge carrier traps and recombination centers [9,14,16–19]. Some limitation also stems from recombination at the buffer/absorber interface in particular for larger bandgap, sulfur rich CZTS due to cliff-like conduction band alignment [9,14].

Capacitance-based techniques such as drive level capacitance profiling (DLCP), thermal admittance (TAS) and impedance (IS) spectroscopy, as well as a more routine capacitance-voltage profiling method (CV), are suitable for both defect analysis and study of the parasitic resistance and capacitance. That is why these methods are widely used for the analysis of CZTS(Se) thin film solar cells [20–28]. The question is how results from these measurements, often performed in dark condition and at low temperature, are influenced by light irradiation and how they relate to IV performance under solar cell operating conditions.

TAS has become a conventional method for the direct evaluation of defect levels in CZTS(Se) by means of comparison of the activation energies extracted from the Arrhenius plot of the inflection frequencies with the theoretically determined energy levels of the defects [20,23,28]. However, there is an alternative opinion that the admittance signal is heavily influenced by parasitic series resistance, questioning the reliability of the bulk defects analysis by TAS. For instance, it was claimed [29,30] that the low-temperature step in a capacitance-frequency (C-f) spectrum is related to a temperature variation of the series resistance, R_s . In that case, the main contribution to the total R_s was assumed to be from the back contact interface [31]. Thus, in order to exclude the effect of the parasitic R_s the TAS results require careful interpretation. That could be done, for example, by comparison of the R_s activation energies extracted from temperature dependent current-voltage measurements (JVT) and those obtained from the capacitance-frequency spectrum [29,30].

A more detailed information regarding parasitic losses in the device could be obtained by fitting of the raw impedance data, usually presented as a Nyquist plot, with an equivalent circuit [20,24,32,33]. This approach provides an estimation of the particular values of both the junction parameters and parasitic elements. Opinions regarding optimal equivalent circuit for CZTS(Se) are divided: namely some studies assume a presence of only diode R - C network and parasitic R_s [20,29,34,35], while others propose more advanced models [24,32,33]. Another possible reason for TAS data

misinterpretation is a metastable behavior of the CZTS(Se) solar cells manifesting itself in a variation of JV parameters after light soaking [36–38]. Therefore the TAS experiments could be also influenced by prior light or bias exposure, i.e. carrier injection regime, of the samples. However, just one recent study considers the metastabilities specifically regarding the TAS method [39]. In that work, a single capacitance step was observed in a relaxed device, while a second step appeared after carrier injection by forward biasing. A comparison with possible changes in the room temperature light JV between the two states was lacking.

Thus, the aim of this study is the investigation of the effect of light pre-treatment on the electrical properties of CZTSSe solar cells by means of current-voltage and capacitance based methods. By using red, blue and white light soaking, the influence from carrier generation in the buffer layer and close to the interface can be separated. We study devices where the room temperature light JV behavior is influenced in different ways by the different wavelength light. We also show that light soaking using any wavelength light causes a shift in activation energies from TAS compared to a relaxed state, but with no difference between the different light sources. We discuss reasons for and implications from this supported by analysis and fitting of impedance spectra to avoid misinterpretations caused by for example high series resistance.

2. Experiment

The procedure for the CZTSSe solar cell fabrication has been described in a previous publication from our group [40], where the devices were prepared using different precursors such as CZTS, CZTSe and bilayer CZTS/CZTSe. Here we focus only on best-performance devices, namely those obtained by sulfo-selenization of the magnetron co-sputtered CZTSe precursor. Briefly, the fabrication procedure was as follows. The CuZnSnSe precursor of 1.2 μm thickness was co-sputtered using a Lesker CMS-18 sputter system in an Ar atmosphere from compound targets, CuSe, SnSe, and ZnSe. Samples were annealed for 3 min at 560 $^{\circ}\text{C}$ in a graphite box containing 5-mg and 50-mg of solid elemental sulfur and selenium, respectively. Absorbers were air annealed at a temperature of 300 $^{\circ}\text{C}$, for 10 min., and then etched in KCN, followed by chemical bath deposition of a 60 nm CdS layer. The devices were finished by sputter deposition of i-ZnO (80 nm)/Al:ZnO (210 nm) window layer and evaporation of Ni/Al/Ni front contacts. Finally, 0.5 cm^2 solar cells were defined by mechanical scribing.

The details regarding cross-sectional SEM study, chemical composition analysis, quantum-efficiency (QE) measurements and estimation of the band gap from QE can

be found elsewhere [40]. The room-temperature photoluminescence (PL) spectra were measured by Renishaw inVia system with a 532 nm excitation.

The electrical connection between samples and measuring equipment was provided by aluminum wire (25 μm diameter) ultrasonically bonded with the help of Kulicke & Soffa 4526 wedge wire bonder to a Ni/Al/Ni front contact and by regular copper wire indium-soldered to the Mo back contact (see figure 1S in supplementary material for the details).

Temperature dependent electrical measurements were performed in a liquid nitrogen cryostat connected to a Lakeshore 325 temperature controller in a temperature range from 100 to 310 K. A silicon diode temperature sensor was mounted on the top of a Mo coated glass slide with the same thickness and size as a sample nearby.

Dark and light JVT measurements were carried out by Keithley 2041 in the voltage range from -0.5 to 1.0 V, a LSC-03MD07 RGBW (red, green, blue and white) light-emitting diode (LED) was used as a light source and its intensity was calibrated according to the short-circuit current density (J_{sc}) previously measured with Newport 1.5 AM solar simulator at room temperature.

The series, and shunt resistance (R_{sh}), ideality factor (n) and reverse saturation current (J_0) were extracted from JVT by using analysis procedures described elsewhere [41].

The DLCP and frequency dependent admittance were measured using an Agilent 4284A LCR meter under dark conditions for the relaxed samples. The DLCP experiment were carried out under several frequencies of 10^3 , 10^4 , and 10^5 Hz, also AC voltage amplitude ranging from 0.01 to 0.1 V rms was additionally applied to the samples. Keeping in mind the previously reported effect of the forward biasing on the capacitance measurements [39] the DLCP spectra were recorded only for the reverse DC bias, e.g. from 0 to -0.5 V, and separately from JVT runs. A more detailed description of the proposed algorithm for the electrical characterization of the metastable CuZnSnSSe solar cells is presented in Supplemental material. The net doping concentration from DLCP profiles were calculated using the standard approach [42].

The admittance vs frequency dependencies were measured with AC voltage 30 mV rms for a frequency range from 10^2 to 10^6 Hz in standard mode, i.e. no DC bias, and under reverse DC bias of -0.5 V.

In this study the following light pre-treatments were considered: white, red (635 nm LED) and blue (450 nm LED) light soaking (LS). A different-wavelength light was supplied by the different subpixels of the RGBW LED. The pre-treatments of the samples were provided by 15 min LS of

the solar cells. Additionally, during the temperature dependent experiments, the light was also applied, and interrupted only for the measurements at certain temperature points. It should be noted that the above mentioned duration of the light pre-treatments has been chosen because prior 1.5 AM light soaking experiment showed saturation of the solar cells parameters, i.e. efficiency, J_{sc} , V_{oc} and fill factor (FF), after 15 min.

2. Results and discussion

The chemical composition of the samples was 0.41, 0.37 and 1.88 for [S]/([Se]+[S]), [Zn]/([Cu] +[Sn]) and [Cu]/[Sn] ratio, respectively. This yields bandgap energy of 1.23 eV calculated from the QE spectrum, whereas the PL peak was observed at about 1.1 eV, see Supplementary figure 2S for details. The difference between band gap estimated from the QE and PL peak energy position could be explained by either the electrostatic potential or bandgap fluctuations in the absorber layer [43].

2.1 Current-voltage analysis

The dark and light JV curves measured for reference and pre-treatment cases at different temperatures are presented in figure 1. Additionally the solar cell parameters at room temperature as well as R_s , R_{sh} , ideality factor and J_0 extracted from dark JV data are listed in table 1. As could be seen from figure 1 and table 1 the white and blue LS cause the most severe degradation in solar cell performance, namely the efficiency drops from 7.6 for the reference case to 6.8 and 7.2% for the white and blue LS. This is due to decrease in V_{oc} and FF, while the J_{sc} is even somewhat higher than for the reference case. The reduction in CdS/CZTSSe solar cell performance with white LS is unexpected since the opposite effect, i.e. enhancement of the efficiency after white LS, has been reported in several studies [2,37,44,45]. There is no clear understanding for what is causing the white LS improvement of solar cells parameters. However taking into account the spike-like conduction band alignment in CdS/CZTSSe heterojunction this effect could be explained by the photo-doping [44,46] of the CdS layer leading to lowered spike barrier to electron transport. As a rule it promotes higher J_{sc} and FF while the V_{oc} may either increase or slightly decrease. The V_{oc} decrease has been attributed to the less compensated interface defects [44]. However, the V_{oc} drop was not decisive for the efficiency limitation in those studies, and in all cases improved solar cell performance was observed. In contrast to results discussed above, in our case, the decreasing V_{oc} after white LS is more pronounced, so we can speculate that the surface recombination is a determining factor leading to the solar cell degradation after white LS.

Table 1. Solar cell parameters of the reference and light pre-treatment cases at $T=298$ K

	J_{sc} , (mA/cm ²)	V_{oc} , (V)	FF	Eff., (%)	R_s , (Ω cm ²)	R_{sh} , (Ω cm ²)	Ideality factor	$J_0 \times 10^{-4}$ (mA/cm ²)
reference	30.9 $\pm$ 0.2	0.46 $\pm$ 0.01	53.2 $\pm$ 0.1	7.6 $\pm$ 0.1	2.27	370	1.68	1.96
white LS	31.7 $\pm$ 0.2	0.43 $\pm$ 0.01	49.8 $\pm$ 0.1	6.8 $\pm$ 0.1	1.84	296	1.70	5.39
blue LS	31.0 $\pm$ 0.2	0.44 $\pm$ 0.01	52.7 $\pm$ 0.1	7.2 $\pm$ 0.1	1.83	301	1.65	5.69
red LS	31.1 $\pm$ 0.2	0.45 $\pm$ 0.01	54.5 $\pm$ 0.1	7.6 $\pm$ 0.1	2.01	322	1.63	3.07

Figure 1. Dark and light JV dependencies of the reference and light pre-treatment cases measured at different temperatures: a, d-298 K, b, e-230 K and c, f-182 K.

This speculation is supported by results obtained by the LS with blue light, which is absorbed mostly in the buffer layer. In particular, as could be seen from the room-temperature dark JV (figure 1(a)) the blue and white LS curves are almost identical showing higher forward current and lower R_s than the reference. Also, both blue and white LS pre-treatments lead to increasing J_0 which could be considered as evidence of enhanced recombination.

The red LS shows the opposite effect to other LS pre-treatments. In particular, despite a slight decrease in V_{oc} , the efficiency of the solar cell remains the same as for reference measurements due to a slightly increased FF.

As could be seen from figure 1 (b, c, e and f) the forward current drops with decreasing temperature due to reduced concentration of the free carriers. However, the white LS treatments lead to significant increase in forward current at low temperature, intuitively suggesting that a photo-doping of both buffer and absorber layer takes place. This assumption seems reasonable since the forward current increase was also observed, though to a lesser extent than white LS, in cases of blue and red LS.

The V_{oc} temperature dependencies (figure 2) were analyzed according to the conventional approach [41] by considering the linear extrapolation to $T=0$ K of the high-temperature data, namely from 260 to 310 K, where the ideality factor is almost temperature-independent, see Supplementary figure 3S for details.

Figure 2. Temperature dependence of V_{oc} with a linear extrapolation to $T=0$ K. The inset shows the high temperature range used for extrapolation.

The extrapolation gives a value of about 1.05 eV for reference measurements which is less than the bandgap of

1.23 eV of the absorber. Moreover, this is also smaller than the PL peak energy position of 1.1 eV. This implies substantial interface recombination in the solar cells.

Additionally, to verify the assumption above, the temperature dependencies of the ideality factor and reverse saturation current extracted from reference dark JVT were analyzed according to the approach in ref. [47] implying tunneling enhanced interface recombination. The temperature-dependent ideality factor data shows good correlation with tunneling enhanced interface recombination model which allows calculation of a characteristic tunneling energy E_{00} of 47 meV, see supplementary figure 4S. This value is only slightly higher than those reported in ref. [38,47] for $\approx 7\%$ efficiency CZTSSe solar cells and much lower than E_{00} calculated in [48] for low-performance devices. Calculation from $n \ln(J_0)$ vs $1/k_b T$ plot gives activation energy E_a of 1.4 eV, see supplementary figure 5S, which is about 0.2 eV higher than that obtained in ref. [38,47]. Note that due to scattering in low-temperature n and J_0 data the above mentioned analysis were performed for the temperature range from 170 to 300 K. Nevertheless, the analysis of the temperature dependencies of ideality factor and reverse saturation current confirms our assumption regarding high interface recombination.

In contrast to the substantial effect of LS observed for room-temperature parameters of the device (table 1) the V_{oc} vs. T activation energy is almost insensitive to blue and white LS treatments, while only red LS shows a slightly higher

value of 1.08 eV, suggesting a lower rate of interface recombination (figure 2). It is difficult to make more specific conclusions from V_{oc} temperature dependencies since one needs to consider jointly a complex behavior of the interface defects and a band alignment modification after LS. Thus at this stage, we can only note that red LS causes, a potentially insignificant, reduction in the interface recombination.

2.1 DLCP profiling

The assumption that high and low-temperature photo-doping of the materials under LS takes place could be verified, though in this case only in the absorber side of the heterojunction, by direct evaluation of the net doping concentration (N) from CV and DLCP. However, here we focus on the DLCP data since this method is primarily sensitive to bulk shallow defects and thus provides more reliable results than CV profiling [42]. At the same time the DLCP signal is highly dependent not only on temperature but also on measurement frequency [42]. Therefore to provide more complete information regarding response of the shallow defects to LS at the different temperatures the DLCP spectra were recorded with three different frequencies, namely 10^3 , 10^4 , and 10^5 Hz. In order to discuss the trend in N we consider doping concentration corresponding to the minimal distance point on the profile, i.e. zero bias condition. As could be seen from figure 3 (a, b, e, f, i and j), in a case of reference measurements, N decreased about two times with temperature variation from 298 to 230 K

Figure 3. DLCP profiles at different temperatures. The correspondent measurement frequency f is presented on figures.

regardless of frequency. However, with further temperature drop down to 140 K, the high-frequency DLCP spectra became less temperature-sensitive figure 3 (c, d, g and h), while spectra measured with low-frequency of 10^3 Hz shows a clear decreasing trend, figure 3 (k and l). At the same time, the depletion width monotonically increases in the low-temperature range for all cases of measurement frequency. Thus, it is possible to conclude that there is no complete freeze-out of the free carriers in this temperature range, i.e. from 180 to 140 K, even though, no dramatic change in the net doping is observed [49].

In a case of low frequency measurements of 10^3 Hz, the depletion width is sensitive to the voltage bias even at low temperature, figure 3 (k and l). However, at the temperatures close to 140 K, higher measurement frequency of 10^4 Hz makes the depletion width almost insensitive to the reverse voltage sweep (i.e. no variation at distance scale), figure 3 (h). The temperature range where the depletion width shows no response to the reverse voltage is expanded to about 180 K with further increasing of frequency up to 10^5 Hz, figure 3 (c and d). The low sensitivity of the capacitance, and hence depletion width, to the reverse bias could be considered as an indication of Fermi level pinning at the interface due to the presence of donor-like defects [50,51].

The white LS at $T=298$ K led to an increase in net doping by about a factor of 1.4 for all measurement frequencies and the red and blue LS showed similar trend, figure 3 (a, e and i). The difference between net doping concentrations measured for the reference and LS cases became more pronounced at lower temperatures. In particular, at the $T=230$ K, the LS maintains the net doping concentration at a level higher than roughly $4 \times 10^{17} \text{ cm}^{-3}$, while in a reference case it is as low as about $1 \times 10^{17} \text{ cm}^{-3}$, figure 3 (b, f and j). Such a substantial increase of the net doping concentration implies the presence of the neutral defects which could be ionized by illumination. As follows from figure 3 white and blue LS doping profiles are very similar with respect to both shape and absolute values, while red LS doping profiles give lower doping concentrations over the entire temperature range. We expect 450 nm blue light is absorbed mostly by the CdS buffer with some penetration through to the absorber-buffer interface, while 635 nm red light is absorbed only in the absorber layer. Thus we can speculate that light absorption in the buffer layer provides higher contribution to overall doping concentration than if the light absorption is limited to the absorber layer

2.2 Capacitance-frequency dependencies and TAS activation energies.

The capacitance-frequency (C-f) spectra are presented in figure 4. As can be seen from figure 4 (a) the reference spectra show typical CZTSSe solar cell behavior, namely capacitance decrease with frequency increase. The overall capacitance gradually drops with temperature in both low and high frequency ranges.

Figure 4. The capacitance-frequency (C-f) spectra for the reference (a) and LS cases: (b) - white, (c)-blue and (d)-red LS.

At the intermediate temperature range, the transition from depletion capacitance (C_d), i.e. low-frequency plateau, to the geometrical capacitance (C_g) plateau at high frequency, is accompanied by two steps on the C-f spectra. In a case of low-temperature spectra the C_g plateau stretches practically the entire frequency range and capacitance is almost insensitive to the frequency variation suggesting dielectric freeze-out of the free carriers. As follows from figure 4 (b) the white LS significantly changes C-f spectra. In particular, at the low-frequency range there is a crossover of the high and low-temperature capacitance curves.

In contrast to reference data, the C_d is weakly dependent on temperature decrease and remains as high as at room temperature. Thus, relative to reference data, the C_g dielectric freeze-out plateau shrinks and the range of the capacitance variation with frequency is much wider even at the lowest temperatures, which is also reflected in a much higher DLCP net doping (figure 3). However, similarly to the reference measurements, the two-step curvature of the C-f spectra still takes place. The blue LS C-f spectra are very similar to white LS data, while red LS spectra show higher C_d for both low and high-temperature measurements.

The TAS activation energies (E) can be calculated by fitting of the Arrhenius plot given by the following equation [20]:

$$w_0 = 2x_0 T^2 \exp\left(\frac{\xi_0 E}{k_b T}\right) \quad (1)$$

where ξ_0 is the temperature-independent thermal emission prefactor and ω_0 is the inflection point frequency determined for each temperature from the maximum in frequency dependencies of $-w(dC/dw)$ derivative.

In a case of the reference measurements in the intermediate temperature range, the $-w(dC/dw)$ vs. frequency plot reveals two peaks at low and high frequencies, for convenience these peaks are referred as P1 and P2, correspondingly (see figure 5(a)). Both peaks are shifted with temperature, so that in the low-temperature range only the P2 peak is observed, whereas at high-temperatures the P2 peak is beyond the maximal frequency limit, thus only the P1 peak is presented on the plot. It should be noted that in contrast to ref. [39], where the relaxed sample exhibits a single capacitance step and a second capacitance step appears only after the carrier injection pretreatment, we initially observed two capacitance signatures for the relaxed samples, and LS lead only to their shift on the frequency scale. Thus, the appearance of the additional capacitance steps due to metastable behavior in CZTSSe solar cells cannot be considered as a common trend.

Figure 5. Capacitance derivative frequency dependencies at different temperatures, reference (a) and LS cases: (b) - white, (c)-blue and (d)-red LS.

Arrhenius plots of the ω_0 inflection frequencies determined from the reference $-w(dC/dw)$ spectra shows activation energies of $E_1=220$ meV and $E_2=150$ meV for the P1 and P2 peak, correspondingly, figure 6.

Predictably, the perturbations in capacitance derivative spectra after white LS discussed above lead to significant

changes in both activation energies, namely, E_1 and E_2 are reduced to 131 and 107 meV respectively, while similar ω_0 for all of the LS cases (figure 6 (b, c and d)) yield similar E_1 and E_2 activation energies (figure 6 (b, c and d)).

Figure 6. Arrhenius plot of the ω_0 inflection frequencies for reference (a) and LS cases: (b) - white, (c)-blue and (d)-red LS. Open and filled symbols correspond to zero and reverse DC bias measurements respectively; 1 and 2 subscripts at the activation energies E and prefactor ξ correspond to the P1 and P2 peaks on capacitance derivative spectra, respectively, and subscript “b” denotes DC bias measurements.

The C-f measurements with -0.5 V reverse bias (figure 7) were performed to estimate the effect of interface states on the capacitance steps [50,51].

Figure 7. Capacitance derivative frequency dependencies for admittance data measured at $T=163$ K with no bias (open circles) and with -0.5 V reverse bias (solid circles); reference spectra (a), LS cases: (b) - white, (c)-blue and (d)-red LS.

The reference measurements with reverse bias reveal a drop in absolute value of the capacitance derivative with respect to no bias spectra at the low-frequency range (figure 7 (a)), whereas at the high-frequency range the spectra showed good correlation. A small shift toward higher frequencies of the peak maximums was observed, though it did not lead to any significant changes in TAS activation energies: the Arrhenius plot yields $E_{1(a)}=222$ meV and $E_{2(b)}=149$ meV for bias measurements, figure 6(a). It should be noted that peak P2 (i.e. E_2 activation energy) corresponds to the frequency range where capacitance is almost insensitive to the reverse bias, figure 6S.

Similarly to reference data, the TAS measurements under reverse bias after LS show a drop in the absolute value of the capacitance derivative figure 7 (b, c and d). However the peaks shift is less evident, and hence expectedly led to similar activation energies for the no bias and reverse bias TAS experiments, figure 6 (b, c and d).

As was discussed in the introduction the reliable interpretation of the TAS activation energies is possible only through careful evaluation of the parasitic series resistance and charge transport barriers, which will be presented in the next subsection.

2.3 Parasitic series resistance and charge transport barriers

This section is divided into two parts. The first part concerns possible parasitic series resistance, as seen from JVT in the DC case. The second part concerns equivalent circuit modeling of impedance data as a tool to evaluate parasitic charge transport barriers. This is followed by section 2.4 where activation energies from TAS discussed above are interpreted based on the evaluation of parasitic circuit elements.

2.3.1 Series resistance

We observed a decrease in current in the low-temperature range (figure 1 (b, c, e and f)). This has usually been associated either with freeze-out of bulk defects [21,52] or non-ohmic back contact [20,32] resulting in increasing R_s . In our case, the drastically rising R_s could be clearly seen from its temperature dependence presented in figure 8.

According to widely-used thermionic emission model [20,22,23,53], the temperature dependencies of R_s can be described as $R_s(T) = R_0 + k_b/(qAT) \exp(E/(k_bT))$ here A is the effective Richardson constant and E activation energy due to the barrier.

The $\ln(R_sT)$ vs $1000/T$ dependencies shows a three-region behavior similar to results obtained in ref. [20]. We do not explain the three-region behavior of the R_s temperature

dependencies since one needs to consider different models of the charge transport in the absorber material [54] as well as possible influence of back contact barrier [32]. The intermediate temperature range, i.e. from 240 to 150 K, is most important for the cross-comparison with admittance data and therefore in further discussions we will use activation energies and R_s absolute values corresponding to this range.

Figure 8. Temperature dependencies of series resistance extracted from JVT with calculated activation energies (E); ref and wLS superscript denotes reference and white LS cases, respectively. Due to the close values to white LS case, the activation energies for the red and blue LS are not shown.

The Arrhenius plot yields activation energy of $E^{\text{ref}}=184$ meV and $E^{\text{wLS}}=123$ meV for reference and white LS cases, respectively. The blue and red LS show very similar effect on R_s temperature dependence as white LS, as manifested in almost identical activation energies and absolute values. Since the drastic increase of the R_s is in the same temperature range (figure 8) as the E_1 and E_2 TAS activation energies were observed (figure 6), it is necessary to verify whether the capacitance steps are related to high R_s . To do so, similarly to ref. [29], the TAS activation energies were compared with R_s activation energy extracted from JVT measurements.

As could be seen from figure 6 (a) and 8 there is no considerable correlation between TAS ($E_1=220$ meV and $E_2=150$ meV) and R_s ($E^{\text{ref}}=184$ meV) activation energies calculated for the reference measurements.

In the case of white LS, an analogous comparison shows a noticeable correlation between R_s activation energy $E^{\text{wLS}}=123$ meV and $E_1=131$ meV TAS activation energy (figure 6 (b)). The same trend was observed for the red and blue LS cases. However, despite the correlation of the E_1 with R_s activation energies in a case of LS, it seems unlikely that the main capacitance step is due to parasitic series resistance, since we observed quite high free carrier concentration with DLCP measurements (figure 3). Besides that, the inflection point related to E_1 activation energy, i.e. the P1 peak, has been observed at the low-frequency range

where the capacitance is sensitive to both temperature and frequency (figure 6). Thus, despite high R_s we cannot relate it to the capacitance steps observed on C-f dependencies.

2.3.2 Impedance spectroscopy for charge transport barriers evaluation

As was shown above, the presence of a parasitic charge transport barrier in the device is highly probable. In the equivalent circuit, such a barrier appears as R_1 - C_1 pair connected in series to R_j - C_j network representing the junction. In this case, according to the impedance theory, the Nyquist plot comprises a main semi-circle of the junction and a supplementary semicircle of the parasitic R_1 - C_1 pair, figure 9 (a).

Figure 9. Equivalent circuit models, (a)-equivalent circuits for the Model 1 (M1) with Nyquist plot, dashed line shows impedance for the circuit with a single R - C network. (b) -equivalent circuits for the Model 2 (M2).

The Nyquist plots of the impedance data measured at different temperatures are presented in figure 10. As seen in figure 10 (a), the room temperature Nyquist plot for the reference measurements gives a symmetrical semicircle. As the temperature decrease, the curvature of the Nyquist plot in the high-frequency range forms a tail that could be considered as an additional semicircle partially overlapping with the main semicircle, figure 10 (b). In turn, according to the equivalent circuit (figure 9 (a)), the additional semicircle corresponds to the parasitic R - C network. With further temperature decrease, the tail stretches towards higher $\text{Re}(Z)$ values and shows strong frequency dependence (figure 10 (c)) indicating increases in both resistive and capacitive components of the parasitic R - C network.

In the high-frequency range, the Nyquist plot for the impedance data measured after white LS at room temperature behaves similarly to that of the relaxed state. However, at the lower temperatures there is a substantial difference between them, reflected in the reduced high-frequency tail on the

white LS impedance. It should be noted that this trend is common for all LS cases.

The disagreement between white LS and reference data at lower temperatures was observed not only for the high-frequency parasitic semicircle, but also for the main semicircle, figure 10 (c). The blue and red LS show similar trends in Nyquist plots as those observed for white LS: the only difference is that the radius for the main semicircle is larger in a case of blue and red LS.

As was mentioned above, the room-temperature impedance spectra of the reference and after LS are almost identical in the high-frequency range, while a frequency decrease leads to a growing discrepancy between them. This is especially evident at the lowest frequencies where the Nyquist curve is twisted in a clockwise direction suggesting the presence of the tilted semicircle or part of a loop. With the temperature decrease the low-frequency feature is not so noticeable, but the twisted shape of the Nyquist curve remains clear. The so-called low-frequency “inductive loop” has been commonly observed in perovskite solar cells [55,56] under illumination or bias and has been associated with charge accumulation at the transport layer/absorber interface. With regards to chalcopyrite solar cells, as far as we know, the “inductive” behavior of the impedance frequency dependencies was reported only in ref. [57], which considers low-performance CIGS solar cells under bias. In that study, the appearance of the “inductive loop” was attributed to the presence of the donor-like defects inducing the inverse electric field at the CdS/CIGS interface. In the case of CZTS(Se) solar cells, despite many studies on admittance analysis, the low-frequency “inductive loop” has not been previously revealed. This could be due to the lack of experiments dealing with light-soaking or biasing. However, one recent study [58] reports the observation of the “inductive loop” on the impedance spectra of $\text{Cu}_2\text{BaSnS}_4$ solar cells under forward bias. In that study, similarly to ref.[57], the “inductive loop” was associated with deep traps at the buffer/absorber interface.

The impedance signal exhibits a complex behavior with temperature decrease and LS, so it is insufficient to consider simple equivalent circuits composed of only R_s and R_j - C_j junction elements, although such simple circuits were used in several studies [20,29,34,35]. Moreover, as was shown in studies [22,24,27,32], the appropriate equivalent circuit models for CZTSSe solar cells should include at least an additional R - C element associated with a back contact barrier. Thus, to describe the impedance signal we considered two equivalent circuit models, namely Model 1 which includes R_s series resistance, R_1 - C_1 pair intending to fit high frequency tail and R_j - C_j junction network figure 9 (a).

Figure 10. The impedance spectra (Nyquist plot) for different temperatures (symbols): (a)- 298 K, (b)- 230 K and (c)- 182 K with the results of fitting (lines), bottom left panels represents high-frequency region of the impedance spectra, right-column panels show fittings deviation in impedance modulus for the Model 1 and 2

This model was used in previous studies [24,32,33], and corresponds to the ideal p-n junction while only back contact barrier and series resistance are involved as a parasitic element. The second Model 2 (figure 9 (b)) is similar to Model 1 with the difference that it considers the trap state within the p-n junction, and as shown in ref. [32], this model has worked quite well for CZTS solar cells. Also, since it was shown in ref. [33] that constant phase element (CPE) describes well the imperfection of the p-n junction we consider impedance $Z_{CPE_{j1}}$ of CPE $Z_{CPE_{j1}} = ((j\omega)^{p_{j1}} Q_{j1})^{-1}$, where Q_{j1} is a frequency independent constant and p_{j1} is a dimensionless parameter instead of the “pure” capacitance C_j in the Model 1. In the

case of LS impedance data, to describe low-frequency “inductive” loop, analogously to ref. [57], we used an additional “negative” CPE_{j2} $Z_{CPE_{j2}} = ((j\omega)^{p_{j2}} Q_{j2})^{-1}$, which implies that that the p_{j2} factor is varied in the range from -1 to 0.

Model 1 shows a reasonable fit for the room-temperature reference spectra, while with the temperature decrease there is a considerable disagreement between modeled signal and experimental data, figure 10. This is mainly due to a more pronounced high-frequency tail at lower temperatures. The calculated values of the circuit elements are listed in table 1S (Supplementary materials), and in the case of fitting of the reference data with Model 1 they demonstrate adequate temperature dependencies: namely, increase in absolute

values of the resistive components (R_s , R_i and R_j) and decrease in capacitive elements (C_i and C_j). This is consistent with the increasing series resistance R_s calculated from JVT and decreasing low-frequency capacitance on C-f spectra, and also correlates with the drop in net doping concentration observed on DLCP profiles. However in the case of LS data the fitting with Model 1 gives notable deviation from experimental impedance data even for the room-temperature spectra. This is an expected result since, in addition to high-frequency feature, the LS spectra show the “inductive” low-frequency loop.

The application of Model 2 to the reference data significantly reduces the fitting error, providing an almost perfect fit for the room-temperature spectrum, and deviation less than about 5% for the low-temperature spectra, figure 10. The extracted values of the circuit elements and their variation with temperature are, in general, consistent with the fitting results reported earlier for the CZTS solar cells [32]. In particular, the C_i capacitance is weakly temperature-dependent and dominate over Q_{j1} , while all resistive components (R_s , R_i , R_1 and R_j) drastically increase with temperature decrease (Table 1S).

Model 2 also remarkably improves the fit for the LS data yielding nearly ideal fitting for the “inductive” low-frequency loop and acceptable deviation of the modeled signal from experimental data in the high-frequency range, figure 10. In particular, as could be seen from figure 10, in the case of high-temperature data, the deviation does not exceed 1% for the broad frequency range. Only at high frequency the deviation is slightly higher, namely of about 2.5 %. A similar trend was observed for low-temperature data, though the deviation at high frequency became higher, almost reaching 4%. This insignificant disagreement at is due to the higher-frequency tail which cannot be perfectly fitted to Model 2.

In contrast to reference data, no trends for temperature dependencies of the capacitances extracted from LS spectra were observed. This could be explained by the almost temperature-insensitive overall capacitance of the sample and hence DLCP net doping concentration.

It is worth considering the possible origin of the low and high-frequency features on the impedance spectra in more detail, since they indicate the presence of the parasitic elements in the solar cells. The conventional interpretation refers to a high-frequency tail, and thus additional R - C element (R_1 - C_1 pair here), to the back contact barrier at the $\text{MoS}_2(\text{Se}_2)/\text{CZTSSe}$ interface [24,32,33]. However, the high-frequency tail is very sensitive to the LS treatments. In the cases of white and red LS this effect could be due to the changes in free carrier concentration in the whole absorber

layer and specifically at the $\text{MoS}_2(\text{Se}_2)/\text{CZTSSe}$ interface. At the same time, the latter hardly explains a very similar effect of white and blue LS on the shape of the high-frequency tail. In general, after the blue LS, it is possible to expect hole injection from the buffer and, perhaps, partially from buffer/absorber interface to the absorber, which is reflected in increasing net doping, figure 3. However, it seems doubtful that this could lead to such a substantial distortion at the back contact interface. The sensitivity of the tail to the blue LS allows us to consider a recently proposed model [59] assuming that the buffer layer gives the main effect on the high-frequency impedance signal. Thus, the perturbations in the shape of the high-frequency tail after white and blue LS could be explained by the photo-doping of the buffer CdS layer, while in case of the red LS by the injection of electrons from the absorber to the buffer. Analogously to ref. [59], an additional argument in favor of such an assumption is that, as it is shown in figure 7, the impedance signal is almost insensitive to reverse bias in the high-frequency range. However, within this study, it is difficult to distinguish between the effect of the back contact barrier and buffer on the impedance signal.

Taking into account that “negative” CPE_{j2} provides a reliable fit of the “inductive” low-frequency loop on the LS impedance spectra, and analogously to ref. [57,58], it is possible to speculate that LS treatments generate an “inverse” electric field at the buffer/absorber interface. It is believed [57] that such an electric field is due to the presence of ionized donors at the interface, for instance, interstitial cadmium Cd_i diffusing from CdS buffer layer or selenium vacancy V_{Se} . Therefore, the depressed low-frequency loop at low-temperature range could be due to freeze-out of the donor-like defects [58].

2.4 Interpretation of the TAS activation energies

The results of the above discussed electrical measurements and modeling of the impedance data have led to the following conclusions regarding E_1 and E_2 TAS activation energies.

Taking into account the substantial effect of blue LS on both activation energies they are unlikely related to the high series resistance at the back contact interface.

The main capacitance step, i.e. $E_1=220$ meV activation energy, is most likely related to a bulk acceptor-like defect. This assumption is consistent with high DLCP net doping concentration in the corresponding temperature range (figure 3), thus it is possible to exclude freeze-out of the acceptors. Also, the E_1 activation energy is almost insensitive to reverse

bias (figure 6), this suggests that the capacitance step is due to bulk rather than interface defects [51].

The white and red LS cause photogeneration of free carriers in the absorber layer, and hence metastable change of the Fermi energy, allowing detection of a shallower defect with activation energy of about 130 meV. Thus, taking into account the above assumption regarding Fermi energy variation, almost identical E_1 TAS activation energy after the blue and white LS could be explained by the injection of photogenerated holes from the buffer to the absorber layer. It is hard to attribute these activation energies directly to ionization energies of the particular defects in CZTSSe since the theoretical calculations were performed for pure CZTS or CZTSe [16]. We can only assume that activation energy of 220 meV corresponds to Cu_{Zn}^- antisite, while activation energy of 130 meV is related to a shallower copper vacancy V_{Cu}^- .

In case of the LS experiment, the effect of the high-frequency “inductive loop” on the P1 capacitance step (i.e. E_1 activation energy) cannot be investigated. In particular, the P1 capacitance step was not observed at room temperatures where the “inductive loop” is most severe, and *vice versa* the “inductive loop” is much less evident in the lower-temperature range where E_1 activation energy was determined, figure 5, 6 and 10.

Considering the second capacitance step, i.e. the P2 peak, we can exclude the possibility that it relates to the parasitic R_1 - C_1 pair, since the P2 peak manifests itself at lower frequencies than the high-frequency tail. Thus we cannot completely confirm the hypothesis proposed in ref. [59], that the high-frequency capacitance step originates from the highly resistive buffer layer.

The position of the P2 peak corresponds to the frequency range where capacitance is almost insensitive to reverse bias, figure 7 and 6S. Therefore, in our opinion, the E_2 =150 meV activation energy could correspond to the position of the electron Fermi level pinned below the conduction band edge at the interface [50]. This assumption is consistent with DLCP measurements showing that the depletion width is weakly sensitive to reverse bias in the low-temperature range, figure 3. The reason for the decreasing E_2 after white and red LS to about 110 meV is that the Fermi energy shifts closer to the conduction band due to photogenerated electrons. In the case of blue LS the latter assumption seems somewhat doubtful, since it is expected that blue light is absorbed mostly in the buffer layer. However, a 450 nm blue light could also partially penetrate through the CdS buffer layer providing photoexcitation of electrons at the interface,

therefore blue LS shows a similar effect on the impedance signal as white LS.

It should be noted that due to frequency limitation of the LCR meter the capacitance steps were not observed at room temperature, figure 5 and 6. Thus we were not able to investigate room-temperature metastabilities of the solar cells by considering directly TAS activation energies.

2. Conclusions

In conclusion, we have investigated the metastable behavior of CZTSSe solar cells after light soaking, which manifest itself not only in a variation of the solar cell parameters at room temperature but also leads to substantial changes in TAS activation energies. Therefore our results support the assumption proposed earlier [39] that prior light or bias exposure of the samples can heavily impact the results of capacitance-based measurements.

As a result of the in-depth electrical analysis, the observed low and high-frequency capacitance steps were assigned to Fermi level pinning below the conduction band and bulk defect, respectively. For the first time, we observed an “inductive” low-frequency loop in the impedance spectra of the CZTSSe solar cells after light soaking. This phenomenon was explained in terms of the presence of light-sensitive interface defects. Also, it was concluded, that these defects are probably responsible for the room-temperature metastable behavior of the CZTSSe solar cells, while the low temperature metastable changes might have a different origin.

Therefore, in case of metastable solar cells, the room-temperature impedance signal of light excited devices must be carefully studied to avoid misinterpretation of the results obtained by widely-used admittance spectroscopy.

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