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# Temperature dependent electrical characterization of thin film $\text{Cu}_2\text{ZnSnSe}_4$ solar cells

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## Abstract

Impedance spectroscopy (IS) and current–voltage characteristics measurements were applied to study properties of a  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) thin film solar cell. IS measurements were done in the frequency range 20 Hz to 10 MHz. The measurement temperature was varied from 10 K to 325 K with a step  $\Delta T = 5$  K. Temperature dependence of  $V_{oc}$  revealed an activation energy of 962 meV, which is in the vicinity of the band gap energy of CZTSe and hence the dominating recombination mechanism in this solar cell is bulk recombination. Different temperature ranges, where electrical properties change, were found. Interface states at grain boundaries with different properties were revealed to play an important role in impedance measurements. These states can be described by introducing a constant phase element in the equivalent circuit.

Keywords:  $\text{Cu}_2\text{ZnSnSe}_4$ , impedance spectroscopy, current–voltage characteristics, grain boundaries

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Quaternary compound  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) with a direct band gap and high absorption coefficient ( $>10^4$ ) [1] is a promising absorber material for photovoltaics. Moreover, CZTSe is a low-cost non-toxic semiconductor material, whose elemental constituents are abundant in the Earth's crust. The current power conversion efficiency record of a CZTSe device is 11.6% [2]. Photovoltaic performance is hindered by a large variety of intrinsic lattice defects, which have influence on optical and electrical properties of solar cells. Little information about the defect structure of CZTSe can be found in the literature.

Defects have been studied by photoluminescence spectroscopy [3–6] and also by capacitive spectroscopy methods. In our previous works [7, 8] we studied so-called monograin solar cells consisting of a microcrystal absorber material,

and different defect levels were detected. In CZTSe two defect states were observed by admittance spectroscopy (AS). The unstable defect state showed activation energies from 87 meV to 100 meV and was attributed to the interface states because the possible change of interface properties with time could alter activation energy. The second state at 74 meV was assumed to belong to  $\text{Cu}_{\text{Zn}}^-$ . These activation energies were found by measuring impedance  $Z$  and phase angle  $\theta$  versus frequency  $f$ , and calculating capacitance  $C$  by employing an equivalent circuit, where a series resistor  $R_s$  is followed by a resistor  $R_p$  and a capacitor connected in parallel, ( $R_s$  and  $R_p$  cover series resistance of a structure, wires, contacts, etc, and shunt resistance of the junction, accordingly). Inverse temperature versus the natural logarithm of angular frequencies  $\omega$  that correspond to a capacitance step showed linear dependence and this was used for activation energy calculation.

Weiss *et al* [9] have studied modelling equivalent circuit responses in kesterite solar cells and found that the evaluation of the admittance data cannot be performed simply with the as-measured capacitance data, as an increasing series resistance with decreasing temperature results in a capacitance step within the  $C$ - $f$  profile. For instance, they suppose that measurements data need to be discarded at higher frequencies and at lower temperatures. In addition, they used current-voltage characteristics ( $I$ - $V$ ) to extract series and shunt resistances, but resistances found by direct current measurements are not perfectly suitable for replacing resistance values of alternating current measurements. Moreover, they used as-measured capacitance (meaning no series resistance exists) and later applied series resistance to it.

Goodman [10] showed that accurate measurement of capacitance requires both  $R_s \ll R_p$  and  $R_s \ll (\omega C)^{-1}$  so that the capacitive impedance is the dominant circuit element. Ordinarily, the quantity  $C$  is assumed to be frequency independent, but in experiments this is not always true; reasons may be, for example, charge relaxation times. In general, such effects tend to disappear with increasing frequency and may place a lower limit on the trustworthy frequency range. Moreover, limitations with respect to measurement equipment may place further restrictions upon the measurement frequency. These restrictions require that the resistance and geometry of the solar cell are suitably chosen.

Fernandes *et al* [11] have studied AS of  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) solar cells and also applied various equivalent circuits to fit measured data. They calculated the deviation between measured and fitted data and found that their fitting of measured data is satisfactory only via a quite complicated model. Usually, the more elements used in an equivalent circuit the better fit found, but in this case the interpretation is impossible or inappropriate. Moreover, Friesen *et al* [12] studied a thin film CdTe solar cell and state that as commonly applied equivalent circuit models consist only of frequency-independent circuit elements they cannot be used to describe the frequency dispersion of a thin film solar cell. They replaced the capacitor with a frequency-dependent non-ideal capacitor, called the constant phase element (CPE). It is generally assumed that non-ideal capacitance behaviour originates from a distribution in the current density due to material inhomogeneity and/or the grain boundaries [12]. The use of a CPE provides a better fitting for a depressed semicircle in the Nyquist plot.

According to our previous temperature-dependent measurements [13], three different temperature ranges, where electrical parameters change, were seen in monograin CZTS solar cells. At very low temperatures ( $T < 40\text{K}$ ) the effective band gap energy  $E_g^*$  and series resistance  $R_s$  showed steep changes and this behaviour was interpreted as hole blocking at a CZTSe/CdS heterojunction. Therefore the interface recombination rate turns out to be very low at  $T < 40\text{K}$ .

Usually, impedance spectroscopy (IS) and AS measurements are conducted at higher temperatures because models are then more easily applied and understood. Unfortunately, at very low temperatures interpreting IS spectra is quite difficult. In this work, we analyze this complicated IS measurements data at very low temperatures and correlate with grain

boundaries properties. Also, IS measurements frequency range limits are shown and results of  $I$ - $V$  measurements and IS for a CZTSe thin film solar cell are presented and analyzed.

## 2. Experiment

A CZTSe absorber for this study was prepared by reactive thermal annealing of a metallic Cu/Sn/Cu/Zn precursor stack deposited by dc magnetron sputtering onto Mo-coated soda lime glass substrates, as described elsewhere in more detail [14]. The CZTSe absorber composition was measured by x-ray fluorescence spectroscopy showing cation ratios of Cu/(Zn + Sn) = 0.69, Zn/Sn = 1.45, Cu/Zn = 1.16 and Cu/Sn = 1.69. The details of the preparation of the thin film solar cell device are given in [15]. The individual solar cell (with dimensions  $3 \times 3\text{mm}^2$ ) used for this study shows power conversion efficiency of  $\eta = 6.6\%$  with  $J_{sc} = 27.2\text{mA cm}^{-2}$ ,  $V_{oc} = 383\text{mV}$  and  $FF = 64\%$ .

For temperature-dependent measurements the selected thin film solar cells were mounted in a closed-cycle He cryostat (Janis).  $I$ - $V$  curves were recorded using a Keithley SourceMeter 2401 with  $100\text{mW cm}^{-2}$  illumination. For a light source a standard 250W halogen lamp with calibrated intensity was used. The impedance spectra curves were recorded using a Wayne Kerr 6500B impedance analyzer. For IS the impedance  $Z$  and phase angle  $\theta$  were both measured as functions of frequency  $f$  and temperature  $T$ . The temperature was varied from 10K to 300K with a step  $\Delta T = 5\text{K}$ . The used frequency was in the range 20 Hz to 10 MHz. In order to maintain the linearity of the response signal, the ac voltage was kept as low as 10 mV. The ac measurements were carried out in the dark and dc biases of 0V and  $-0.5\text{V}$  were used. After each measurement, the real and imaginary parts of the impedance,  $Z'$  and  $-Z''$  respectively, were calculated. Measured data were fitted using the ZView (Scribner, USA) computer program, which gives values for elements used in an equivalent circuit; for example, series resistance,  $R_s$ .

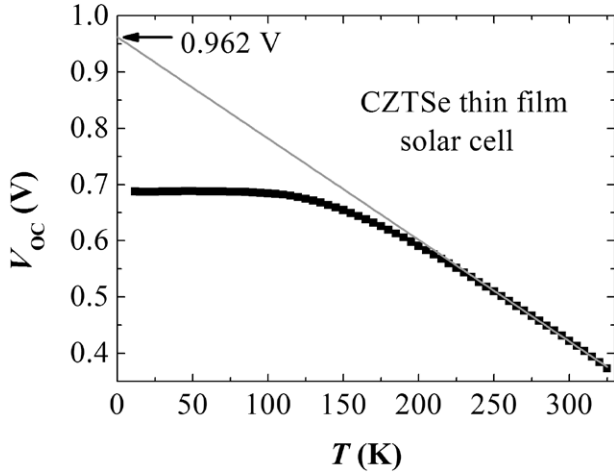
## 3. Results and discussion

The studied solar cell exhibited an efficiency of 6.6%. Temperature dependence of the open circuit voltage ( $V_{oc}$ ) derived from  $I$ - $V$  measurements with varied temperature from  $T = 10\text{K}$  to  $T = 325\text{K}$  was linear in the range 250K to 325K (see figure 1). It is known that the temperature dependence of  $V_{oc}$  near room temperature can be presented as [16, 17]

$$V_{oc} = \frac{E_{A,V_{oc}}}{q} - \frac{nkT}{q} \ln\left(\frac{I_{00}}{I_L}\right), \quad (1)$$

where  $I_L$ ,  $E_{A,V_{oc}}$ ,  $n$ ,  $k$  are the photocurrent, an activation energy, the diode ideality factor and the Boltzmann constant, respectively. The constant  $q$  is the electrical charge of the electron and  $I_{00}$  is obtained from the temperature dependence of the dark saturation current  $I_0$ . In good solar cells  $-I_L \approx I_{sc}$ , where  $I_{sc}$  is a short circuit current.  $I_0$  equals [16, 17]

$$I_0 = I_{00} \exp\left(-\frac{E_{A,V_{oc}}}{nkT}\right) \approx AT^3 \cdot \exp\left(-\frac{E_{A,V_{oc}}}{nkT}\right). \quad (2)$$



**Figure 1.** Temperature dependence of  $V_{oc}$  of a CZTSe thin film solar cell.

In general, the activation energy  $E_{A,V_{oc}}$  and also  $I_{00}$  depend mostly on the dominating recombination mechanism in the solar cell. In the case of bulk recombination  $E_{A,V_{oc}} \approx E_g$ , where  $E_g$  is the band gap energy of the absorber material.

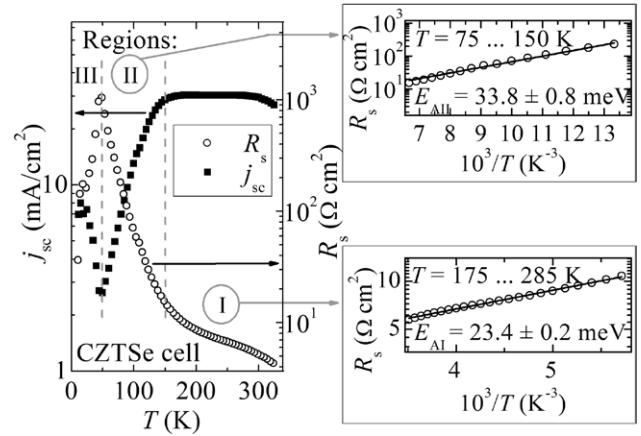
Linear fitting of the temperature dependence of  $V_{oc}$  showed that  $E_{A,V_{oc}} = 962$  meV (see figure 1), which is in good agreement with the band gap energy of CZTSe that is expected to be in the vicinity of 1 eV [4, 18], and hence the dominating recombination mechanism seems to be bulk recombination.

According to the temperature dependence of  $j_{sc}$  (see figure 2) three different temperature regions can be distinguished. Similar behaviour was also seen in CZTS [13]. At temperatures  $T > 150$  K (region I) the series resistance  $R_s$  decreases with increasing temperature, indicating the thermal activation of carriers. In this region,  $R_s$  can be calculated by

$$R_s = R_{s0} \exp(E_A/kT), \quad (3)$$

where  $R_{s0}$  covers all parameters that are temperature-independent and  $E_A$  is an activation energy. Using equation (3), the activation energy  $E_{AI} = 23.4 \pm 0.2$  meV was found in the temperature range 175 K to 285 K (region I). Similar values in kesterites have been published before, for example 29–48 meV [19, 20]. In our sample, the activation energy of 23.4 meV is related to grain boundaries or some shallow acceptor-like defect.

At intermediate temperatures (region II,  $T = 50$  K to 150 K) another thermally activated process appears. Using equation (3), the activation energy  $E_{AII} = 33.8$  meV was found in the temperature range  $T = 75$  K to 150 K. In our previous studies [3, 4, 21] this activation energy was related to potential fluctuations of the valence band edge; it is the energy needed by holes to cross barriers that were created by these potential fluctuations. According to the literature, the root mean square depth of the potential well  $\gamma$  in CZTSe is usually in the range  $\gamma = 20$ –30 meV [3, 4, 21]. At the same time it is shown that in region II, the dependence of the series resistance on temperature changes and a typical Mott's variable-range hopping conduction starts to emerge [22]. This behaviour is expected in all heavily doped materials, where spatial potential fluctuations create deep potential wells for holes. But at the same



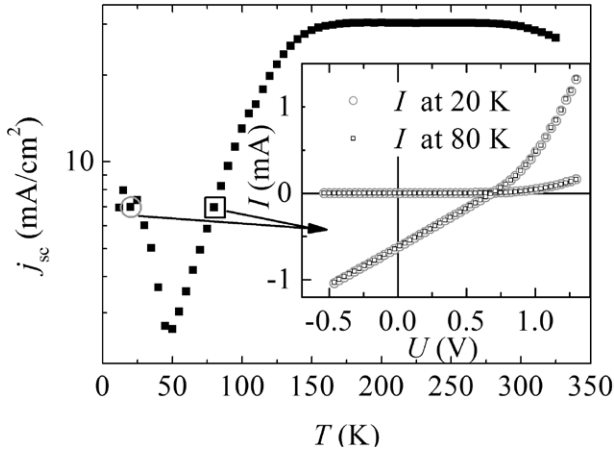
**Figure 2.** Temperature dependence of  $j_{sc}$ . Insets show found activation energies in region I and II.

time, we also expect an increasing role of bulk recombination in region II, as previously seen in CZTS [13]. At low temperatures ( $T \lesssim 150$  K), the carriers, here holes, can occupy shallow acceptor states in the band gap. These states can arise from intrinsic defects or impurities or their interaction. At a sufficiently high concentration of these states, but below the critical Mott concentration, overlapping of carriers wave functions could form a so-called impurity band [23]. In such a case charge carriers can move from one shallow impurity state to another one at its spatial neighbourhood and conduction in the impurity band is expected [22]. These different processes could all be present and therefore we do not focus so much on activation energy here.

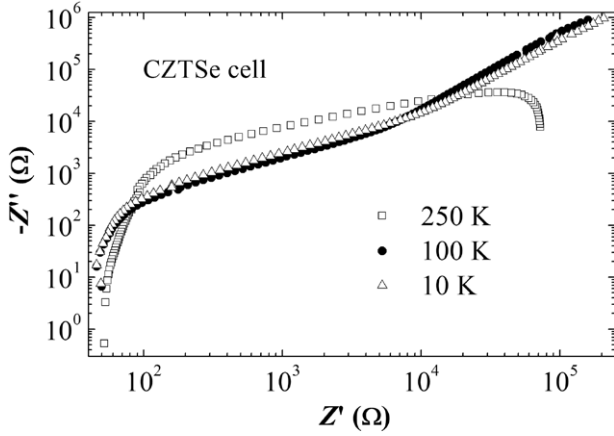
At low temperatures (region III,  $T = 10$  K–50 K) the maximum of series resistance is present. By analyzing  $j_{sc}$  and  $I$ – $V$  graphs (see figure 3), it can be seen that  $I$ – $V$  curves have similar shapes symmetrically to both sides of 50 K. Also, impedance curves have quite similar patterns symmetrically to the temperature of  $T = 50$  K in the Nyquist plot (compare the complex impedances at 10 K and 100 K in figure 4). The sudden drop in resistance below 50 K seems to be related to blocking of the interface recombination. The rapid change in the series resistance can occur because of cooling of the recombination processes: generated holes are not able to tunnel through the potential barrier into the interface region between CZTSe and CdS and therefore the interface recombination rate must be very small at these very low temperatures ( $T = 10$  K–50 K) [13].

IS is a powerful non-destructive tool for characterizing semiconductors. IS detects the ac current response of a system to a small ac voltage signal with varied frequency. The impedance can be calculated by  $Z = V/I$ . From complex impedance the capacitance can be calculated, but this requires a certain equivalent circuit to be known. The temperature dependence of  $Z'$  and  $-Z''$  of the CZTSe thin film solar cell is shown in figure 4.

Our measured impedance curves in the Nyquist plot in the whole temperature range can be fitted by applying an equivalent circuit, where a series resistor is followed by a resistor and a capacitor connected in parallel and followed by additional elements ( $R_{p2}$  and CPE) connected in parallel (circuit



**Figure 3.** Temperature dependence of  $j_{sc}$ . Inset shows  $I$ - $V$  curve shape similarity between both sides of 50 K at different temperatures.

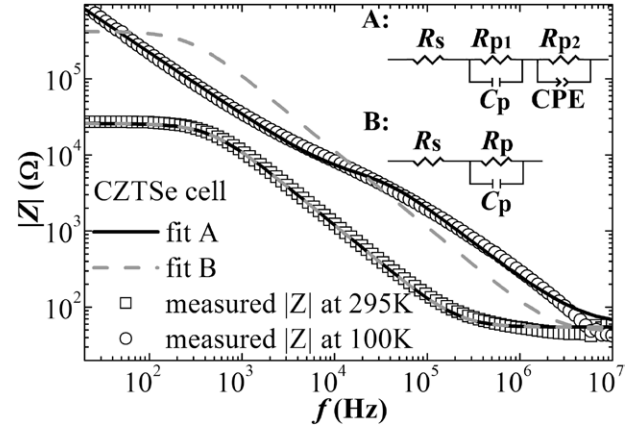


**Figure 4.** Nyquist plots. Selection of impedance curves of the CZTSe thin film solar cell in the logarithmic scale at temperatures 250 K, 100 K and 10 K.

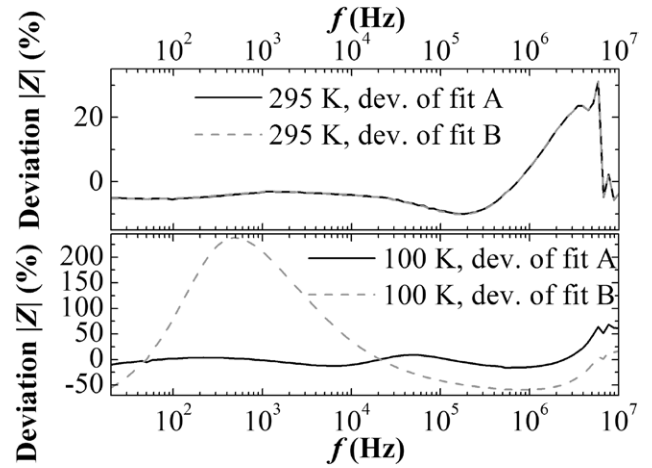
A in figure 5). The used complex impedance of a CPE,  $Z_{CPE}$  is given by

$$Z_{CPE} = \frac{1}{C_{CPE} \cdot (i \cdot \omega)^P}, \quad (4)$$

where  $C_{CPE}$  is equal to capacitance  $C$ , if parameter  $P = 1$ .  $\omega$  stands for angular frequency. But fitting of high temperature IS curves is also satisfactory with an equivalent circuit, where a series resistor is followed by a resistor and a capacitor connected in parallel (circuit B in figure 5). In figure 5 both theoretical fittings and experimental data curves are shown. In figure 6 the deviation between theoretical and experimental impedance data is shown. It is clearly seen that at room temperature there is no difference between fittings with circuits A and B, but the deviation between fitted and measured  $|Z|$  increases at higher frequencies. At low temperatures, i.e.  $T \lesssim 150$  K, the equivalent circuit B was not suitable at all, and the equivalent circuit A fitting deviation of measured  $|Z|$  is enormously high (more than 50%) at quite high frequencies. Obviously, condition  $R_s \ll (\omega C)^{-1}$  [10] is not satisfied at higher frequencies. It was checked by calculations and found



**Figure 5.** Measured impedance of the CZTSe solar cell and fitting results with corresponding equivalent circuits. A better fit was obtained by A. Commonly used equivalent circuit B is not suitable at lower temperatures  $T \lesssim 150$  K. At room temperature no enormous difference was seen.



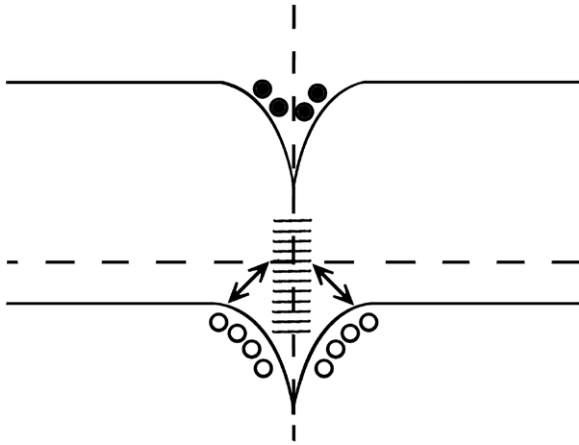
**Figure 6.** Fitting deviations of  $|Z|$  versus frequency at temperatures 295 K and 100 K of the CZTSe solar cell.

that this condition is satisfied at frequencies  $f < 3.7$  MHz at 100 K and at  $f < 250$  kHz at room temperature. Moreover, measurement instrumentation capabilities have limits and affect measurements data. At low frequency, the fitting deviations of  $|Z|$  were not significant. Hence, IS results at higher frequencies are not trustworthy, and wide fitting deviations of  $|Z|$  coincide with neglecting the condition  $R_s \ll (\omega C)^{-1}$ .

At every measured temperature values of the equivalent circuit elements can be found by exploiting the  $Z$  view program for fitting. In turn, the  $R_s$  values can be used to calculate the capacitance. When assuming series inductance to be insignificant or absent, equivalent circuit B can be described by the following equation [24]:

$$Z = R_s + \frac{R_p}{1 + (\omega R_p C)^2} - i \frac{R_p^2 C \omega}{1 + (\omega R_p C)^2}, \quad (5)$$

where  $\omega$ ,  $C$  and  $R_p$  are angular frequency, capacitance and parallel resistance, respectively. After rewriting (5), the capacitance can be found by



**Figure 7.** Grain boundary located between grains in the thin film solar cell. Some interface states are affected at quite low temperatures and these impact fittings of measured data.

$$C = \frac{-Z''}{[(Z' - R_s)^2 + (-Z'')^2] \cdot \omega}, \quad (6)$$

where  $Z'$  and  $-Z''$  are the real and imaginary part of the complex impedance, respectively. Equation (6) can be used for capacitance calculation, if equivalent circuit B is applied for the fittings. In equivalent circuit A, CPE is used and in this case equations (5) and (6) would take a much more complicated form and the calculation of capacitance would not be straightforward. Thus, in the case of our studied CZTSe thin film solar cell capacitance should be derived by using equivalent circuit B and valid results are obtained only at higher temperatures ( $T = 150 \text{ K}$  to  $325 \text{ K}$ ). However, IS results are also beneficial in this low temperature range, because they add complementary or confirmative details about processes.

Temperature dependence of electrical parameters seen by IS in the CZTSe thin film solar cell at  $T \lesssim 150 \text{ K}$  can be explained by grain boundaries, see figure 7. It seems that some interface states at grain boundaries are affected and change electrical properties of the studied cell at low temperatures. These states may not show a real capacitance, but can be explained by CPE in the equivalent circuit due to grain boundaries with different properties. This extra capacity is caused by holes being captured by interface states in grain boundaries, which are below the Fermi level, and released by states, which are above the Fermi level. If the cell is contacted and being electrically disturbed, then the band bending and hence crossing between Fermi level and interface states change. As a result, charging or discharging of these states occurs and capacitance can be detected.

As a result of this kind of capacitance change at low temperatures  $T \lesssim 150 \text{ K}$ , where grain boundary states are affected, we need to add extra elements to our equivalent circuit. At high temperatures ( $T = 150 \text{ K}$ – $325 \text{ K}$ ), where grain boundary states do not contribute to capacitance, both equivalent circuits give excellent results. This low temperature ( $T = 10 \text{ K}$ – $150 \text{ K}$ ) behaviour, which requires the use of CPE and is present in the studied CZTSe thin film solar cells, was not seen in our previous research on monograin solar cells, where the role of grain boundaries was not so notable [7, 8].

## 4. Conclusions

IS and current–voltage characteristics were used for characterizing the CZTSe thin film solar cell. Different temperature ranges where electrical properties change were seen. Fittings of impedance data showed that some interface states at grain boundaries are affected at low temperatures. These states can be described by CPE in equivalent circuits due to grain boundaries with different properties. Linear fitting of temperature dependence of  $V_{oc}$  showed activation energy  $E_A = 962 \text{ meV}$ , which is in good agreement with the band gap of CZTSe. Hence the dominating recombination mechanism seemed to be bulk recombination in the studied thin film solar cell. From temperature dependence of  $j_{sc}$  the activation energies were found. In the temperature range from  $175 \text{ K}$  to  $285 \text{ K}$  the activation energy of  $23.4 \text{ meV}$  is related to the energy needed to cross the grain boundaries or some shallow acceptor-like defect. At intermediate temperatures, from  $75 \text{ K}$  to  $150 \text{ K}$  different processes like carrier localization in potential wells, radiative recombination and Mott's variable-range hopping conduction start to come into effect, showing an activation energy of  $E_{AII} = 33.8 \text{ meV}$ . In conclusion we have shown that temperature dependent impedance and  $I$ – $V$  studies can give a valuable insight into electronic processes related to grain boundaries and interfaces in solar cells.

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