



## Temperature dependent electroreflectance study of $\text{Cu}_2\text{ZnSnSe}_4$ solar cells



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### ABSTRACT

Electroreflectance measurements (ER) of  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) solar cell were performed in the temperature range of  $T=100\text{--}300\text{ K}$ . ER spectra were fitted using the Lorentzian line shape functional form. The broadening parameter did not change with temperature and had very high value of 125 meV. High concentration of charged defects and spatial fluctuations of bandgap energy caused by the presence of both ordered and disordered crystal structures and/or different defect clusters are the main reasons for broadening of the ER spectra. The temperature dependence of the band-gap energy for CZTSe was determined from ER data. The overall shift of the bandgap energy was found to be only about 13 meV from room temperature to  $T=0\text{ K}$ .

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### 1. Introduction

In recent years kesterite  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) thin films have been intensively investigated as a potential low cost absorber for solar cells.  $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$  (CZTSSe) based thin film solar cells have achieved efficiencies as high as 12.6% [1] while CZTSe cells have shown efficiency of 11.6% [2]. However, compared to thin film solar cells with a similar band gap  $E_g$  but based on the related  $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$  absorber, CZTSe cells have lot of additional problems.

It is known from different experiments that kesterites exhibit a disorder in the Cu–Zn layers at  $z=1/4$  and  $z=3/4$  of the unit cell due to  $[\text{Zn}_{\text{Cu}}\text{--}\text{Cu}_{\text{Zn}}]$  antisite defect pairs [3,4]. The presence of Cu–Zn disorder and different defect clusters can significantly reduce the bandgap energy  $E_g$

[5,6]. The coexistence of ordered and disordered structures in  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) was experimentally discovered using low temperature photoluminescence (PL) measurements [7]. It was found that the difference between bandgap energies of ordered and disordered structures is about 80 meV, the latter being smaller. Similar results have been obtained also in CZTSSe (S/Se-ratio of 8%), where using the electroreflectance the room temperature bandgap energy  $E_g$  of ordered and disordered CZTSSe was found to be 1.08 eV and 0.96 eV respectively [8]. In pure CZTSe the Cu–Zn ordering can increase  $E_g$  by 110 meV as compared to fully disordered material and therefore  $E_g$  can be used as an order parameter [9]. The critical temperature for the CZTSe order–disorder transition was found to be about 200 °C [9]. At equilibrium, the CZTSe is completely disordered if the temperature is above 200 °C. Below this critical temperature the equilibrium ordering degree increases continuously and the perfect order is reached only at 0 K. It was found that the room temperature bandgap energy  $E_g$  of ordered and disordered CZTSe is about 1.057 eV and 0.94 eV respectively [9]. Degree of

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Cu–Zn ordering can be changed also by using different cooling rates near the critical temperature after the high temperature treatment [8,10].

It is expected that the total charged defect concentration is lower in ordered CZTSe, but recent PL measurements of CZTSe thin films [9] and also CZTS monograins did not confirm this hypothesis [10]. At the same time, the defect structure and the nature of defect complexes changed with a cooling rate. It is worth to mention that CZTSe with the lowest defect concentration so far and showing an excitonic photoluminescence emission has a room temperature bandgap energy of  $E_g = 1.01$  eV [11] and thus a significant quantity of Cu–Zn disordering. Besides Cu–Zn disordering the bandgap energy depends also on quality and composition of samples. These are the main reasons for a large discrepancy between reported  $E_g$  values of CZTSe in the literature.

Majority of measured CZTSe samples show properties of so-called heavily doped material. The conditions of heavy doping originate from the high concentration of native defects that is often observed in kesterites [12–14]. In a semiconductor with a random distribution of charged donors and acceptors spatial fluctuations of the electrostatic potential are formed. These potential fluctuations will lead to a local perturbation of the band structure, thus broadening the defect level distribution and forming band tails. As a result, the band gap in the heavily doped semiconductor is not well defined and is usually determined by the percolation levels of electrons and holes. This fact introduces additional problems when the bandgap energy is measured using common methods like the absorption or an external quantum efficiency (EQE) spectra. In [14] it was shown that the band gap of CZTSe can be estimated by extrapolation of the low-energy slope of the recorded EQE curve only at temperatures  $T > 250$  K. At lower temperatures EQE starts to decrease and this is related to a localization of generated holes inside deep valence band potential wells. It is obvious that EQE depends not only on the absorption coefficient but also on the ability of generated charge carriers to reach the front and back contacts. At  $T < 250$  K the mobility of holes rapidly decreases due to localization and the bulk recombination through these deep wells increases reducing the overall EQE.

At the same time not only a room temperature band gap is important but also a temperature dependence of  $E_g$ . Recently Choi et. al. [15] published their spectroscopic ellipsometry study of the dependence of the band-gap energy for CZTSe on temperature ranging from 50 to 350 K. Their thin film samples showed a room temperature bandgap energy of  $E_g = 0.97$  eV and according to [9], this low  $E_g$  must be related to high degree of Cu–Zn disordering. It was found that  $E_g$  of CZTSe decreases with increasing temperature, but the variation seems to be relatively small. However, the measurement of the absorber band gap in finished solar cells is often also interesting and probably gives additional information about solar cell properties. For example, in the CdTe/CdS solar cells a formation of  $\text{CdS}_x\text{Te}_{1-x}$  solid solution at the interface was detected in [18]. Moreover, it could be attractive to test a temperature dependence of  $E_g$  on samples with

higher degree of ordering. Many experimental techniques have been applied to measure band gaps of CZTSe cells. One such technique is the electroreflectance spectroscopy (ER). Electroreflectance spectroscopy is staging an important role in determining the electronic structures and probing the optical properties of semiconductors due to its easy implementation and exhibition of relatively sharp spectra without noticeable background even at room temperature. Modulation of the electric field by an AC voltage in a space charge region of a thin film solar cell offers a convenient and non-destructive way to detect critical points within the region of the barrier. Recent room temperature ER measurements of CZTS solar cells [8] proved that this method can really be used for a band gap measurements even in highly doped kesterites. In CZTSe solar cells ER is not used before and no data about the temperature dependence of  $E_g$  in real solar cells is present.

In this paper, we report on temperature dependence of the bandgap energy  $E_g$  in CZTSe thin film solar cells detected by ER.

## 2. Experimental details

CZTSe absorber for this study was prepared by reactive thermal annealing of metallic prepursor stack deposited by DC magnetron sputtering onto Mo coated soda lime glass substrates, as described elsewhere in more detail [20]. The CZTSe absorber composition was measured by X-ray fluorescence spectroscopy showing relative cation composition of Cu=38.0%, Zn=36.7% and Sn=25.3% which results in cation ratios of  $\text{Cu}/(\text{Zn}+\text{Sn})=0.61$ ,  $\text{Zn}/\text{Sn}=1.45$ ,  $\text{Cu}/\text{Zn}=1.04$ , and  $\text{Cu}/\text{Sn}=1.5$ . Highest device performance is reported in this Cu poor Zn rich compositional range and recently even for very Cu poor absorber layers performant devices with especially high Voc values are reported [24]. Solar cells were finished by depositing a CdS buffer layer by chemical bath deposition followed by DC-pulsed sputtered ZnO (50 nm) and  $\text{In}_2\text{O}_3:\text{SnO}_2$  (90/10 wt%; 350 nm,  $R_s=50 \Omega \text{ cm}^{-1}$ ) window layer [21]. Prior to CdS deposition the CZTSe absorber was etched using an oxidizing etching to remove possible ZnSe secondary phases from the surface as reported in [20]. The compositional values presented here were measured prior the specific surface etching because time between surface etching and buffer layer deposition is crucial to avoid surface contamination. Thus a reduction in Zn composition is expected in the final CZTSe absorber layer. The individual solar cell used for this study shows power conversion efficiency of  $\eta=6.6\%$  with  $J_{sc}=28.3 \text{ mA cm}^{-2}$ ,  $V_{oc}=368 \text{ mV}$ , and FF=63%.

For the electroreflectance measurements the DC- and AC-voltages were applied to a solar cell under study via back and front contacts by a pulse generator with frequency of 275 Hz, AC value of  $\pm 0.8$  V and DC component of  $-0.8$  V. Computer controlled grating monochromator SPM-2 ( $f=40$  cm) together with a 250 W quartz-tungsten halogen lamp was used for illumination. The change in reflectance  $\Delta R$  and reflectance  $R$  were both measured using a lock-in amplifier (SR 810) and a Ge detector in the spectral range from 0.8 to 1.5 eV. The solar cell was mounted into a closed-cycle He cryostat to perform

temperature dependent measurements in the range of  $T=100\text{--}300\text{ K}$ .

Electroreflectance can be classified into three categories: weak, intermediate and strong field regimes, depending on the strength of a local electrical field in the junction. In our case the weak field regime seems to be present. ER spectra near the fundamental band-gap energy with a weak field approach can be well fitted with a third derivative functional form (TDFE) given by Aspnes [16]

$$\frac{\Delta R}{R} = \text{Re} \left[ C e^{i\phi} (E - E_g + i\Gamma)^{-m} \right] \quad (1)$$

where  $E$  is the photon energy,  $C$  is an amplitude parameter,  $\phi$  phase parameter,  $E_g$  energy of the bandgap and  $\Gamma$  is a broadening parameter. The exponent  $m$  depends on the type of the critical point and is usually related to the line shape of the dielectric function (e.g., Lorentzian or Gaussian).

### 3. Results and discussion

Temperature dependent ER spectra together with Aspnes fit (Eq. (1)) of CZTSe cell are presented in Fig. 1. It is clearly seen that the spectrum shifts towards higher energies with decreasing temperature, but the shift is very small and the shape of ER peak remains relatively unaffected. This means that the linewidth is determined by the inhomogeneous broadening. Although the spectral fit with Eq. (1) gives good results near the critical point, we still notice some deviation at higher energies, see Fig. 1. This deviation could be an indication of a second critical point at higher energy. For example, in [15] the room temperature  $E_0(C)$  bandgap of CZTSe due to spin-orbit splitting of valence band was found at 1.272 eV. However, our ER signal was too low near this energy and therefore we fitted only the main peak. The overall shape of the main peak is determined by a high concentration of charged defects and spatial fluctuations of the band edge in this compound. As a result the dielectric function will be affected and inhomogeneous broadening mechanisms start to dominate.

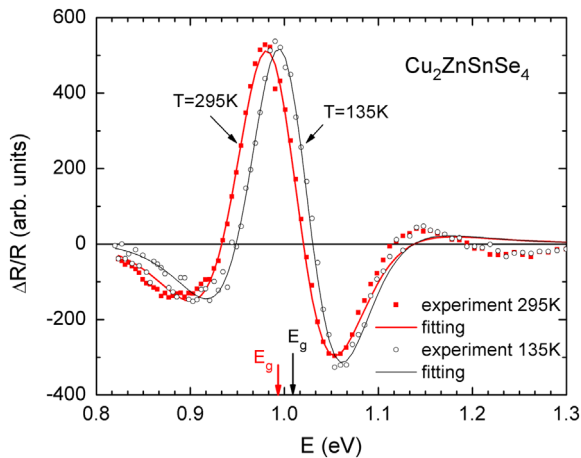


Fig. 1. ER spectra of CZTSe solar cell at temperatures 135 K and 295 K. Dots show the experimental data and continues lines are the fitting results with Eq. (1).

Moreover, the best fit was achieved using remarkably high  $m$  values  $m \geq 3$ . However, according to our calculations the exponent  $m$  mostly determines the line-shape of the ER spectrum far from a critical point and does not affect the spectrum near the bandgap energy  $E_g$ . An average value of the broadening parameter  $\Gamma \approx 125\text{ meV}$  is practically constant over the whole temperature range and one possible explanation is, that not only potential fluctuations, but also the bandgap energy fluctuations due to presence of ordered and disordered structures and/or different defect clusters [5,6,22] are affecting the inhomogeneous broadening. Very similar bandgap energy fluctuations were discovered by PL in the ternary compound  $\text{CuGa}_3\text{Se}_5$  [19] and, as a rule, they lead to an abnormal widening of PL and ER bands. Therefore, the bandgap energy  $E_g$  obtained from ER fittings always represents some average value. Very wide room temperature ER spectra were measured also in CZTSSe by Krämmer et al. [8]. They noticed that, due to inhomogeneous broadening mechanisms, the resulting modulus spectra calculated from ER experiments could be better fitted with a Gaussian lineshape instead of Lorentzian. It seems that this inhomogeneous broadening due to spatial bandgap energy and potential fluctuations is a typical feature in all kesterites and does not depend on the bandgap energy. Unfortunately, ER measurements were not possible at  $T < 100\text{ K}$  because ER signal dropped significantly. At low temperatures holes start to localize in the valence band potential wells and as a result, the series resistance of the solar cell increases considerably [14,23]. This leads to a reduction of an external electric field on a junction and accordingly ER signal drops.

The resulting band gap values for the CZTSe cells are shown in Fig. 2. The temperature dependence of  $E_g$  was fitted with the expression introduced by O'Donnell and Chen [17]:

$$E_g(T) = E_g(0) - S < \hbar\omega > [\coth(\langle \hbar\omega \rangle / 2kT) - 1], \quad (2)$$

where  $E_g(0)$  is the band gap energy at 0 K,  $S$  is a dimensionless coupling constant and  $\langle \hbar\omega \rangle$  represents an average phonon energy. The solid curve in Fig. 2 is the best fit of

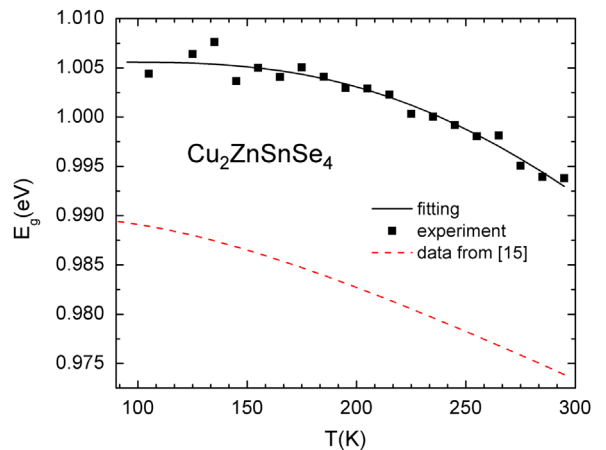


Fig. 2. Bandgap energy values found from ER fittings as a function of temperature. Solid curve is a fitting result with Eq. (2). The dashed curve represents the temperature dependence of bandgap energy of CZTSe according to data from ref. [15].

the  $E_g(T)$  values using Eq. (2) with the fitting parameters  $E_g(0) = 1.006 \pm 0.001$  eV,  $S = 2.0 \pm 0.6$  and  $\langle \hbar\omega \rangle = 85 \pm 13$  meV. The overall shift of  $E_g$  is only about 13 meV from room temperature to  $T=0$  K. Somewhat greater shift was found by Choi et al. [15], see Fig. 2.

#### 4. Conclusion

In conclusion, temperature dependent ER measurements ( $T=100$ – $300$  K) were performed with CZTSe solar cell. All ER spectra were fitted using Aspnes third derivative functional form. High values of the broadening parameter  $\Gamma$  are explained by the high concentration of charged defects and spatial fluctuations of the bandgap energy caused by the presence of both ordered and disordered structures and/or different defect clusters in CZTSe. Temperature dependence of the bandgap energy of CZTSe was determined. The overall shift of the bandgap energy was found to be only about 13 meV from room temperature to  $T=0$  K.

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