Temperature dependent current transport properties in Cu$_2$ZnSnS$_4$ solar cells

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Abstract

Quaternary semiconductor compound Cu$_2$ZnSnS$_4$ (CZTS) is a promising non-toxic absorber material for solar cells made from earth abundant elements. In this study, temperature dependencies ($T = 10$–$300$ K) of current–voltage ($J$–$V$) characteristics and external quantum efficiency (EQE) spectra of CZTS monograin layer solar cells were measured in order to clarify current transport in CZTS that is still not fully understood. Three different temperature ranges can be distinguished from the temperature dependence of the series resistance ($R_s$) obtained from $J$–$V$ measurements and the effective bandgap energy ($E_g$) determined from the EQE spectra. Thermally activated conductivity, Motz’s variable-range hopping conductivity, and very low temperature ($–40$ K) blocking of the interface recombination were observed.

1. Introduction

Multinary semiconductor compounds Cu$_2$ZnSn(S$_x$S$_{1−x}$)$_4$ (CZTSSe) are promising non-toxic absorber materials for solar cells made from earth abundant elements. Currently, the power conversion efficiency record of Cu$_2$ZnSnS$_4$ (CZTS) device is 8.4% [1] and that of CZTSSe device – 12.6% [2]. High series resistance and interface recombination are reported as the main limiting factors in CZTS-based solar cells [3,4]. Hence, almost all basic solar cell parameters are limited by recombination and parasitic losses. Moreover, most of CZTS absorbers used in solar cells show properties of so-called heavily doped semiconductors, where high concentration of charged defects leads to a formation of spatial potential fluctuations [5]. Accordingly, different type of current transport and recombination mechanisms can be observed [6–9].

In CZTS solar cells recombination losses are not only related to the interface between absorber and buffer layers but also to different bulk defects or band tails. The first-principle calculations have been made for CZTS by Chen et al. [10]. They found that the main acceptor defect in CZTS is Cu$_{2zn}$ antisite defect that has a quite deep level at $E_A = 0.12$ eV. This acceptor was also found by admittance spectroscopy [11]. Even deeper acceptor ($E_A = 0.28$ eV) was detected in CZTS by photoluminescence spectroscopy [12]. These quite deep defects can be efficient recombination centers even at temperatures close to room temperature. At the same time, Chen et al. [13] have shown that the compensation between the dominant acceptor defect Cu$_{2zn}$ and the donor defect Sn$_{2zn}$ can significantly decrease the formation energies of the defect clusters (Cu$_{2zn} + $Sn$_{2zn}$ and 2Cu$_{2zn} + $Sn$_{2zn}$) leading to high concentrations of these clusters even in stoichiometric samples. It was shown that the recombination through these defect clusters dominates in most CZTS samples at low temperatures [14]. The presence of different defect complexes in CZTS was also proposed by Huang et al. [15]. According to their calculations these complexes can cause a significant local band gap decrease and boost the recombination.

The temperature-dependent conductivity of polycrystalline CZTS thin films [3,4,6–9] and single crystals [16] has been studied in many papers. However, in real solar cell structures many different recombination channels appear which are not present in bulk CZTS. Therefore, it is extremely interesting to study temperature dependence of these real structures. We already have studied the temperature dependencies of Cu$_2$ZnSnSe$_4$ monograin layer (MGL) solar cells and showed how potential fluctuations change the current transport in these structures [17]. In this study, current–voltage ($J$–$V$) characteristics and external quantum efficiency (EQE) curves were used for characterizing recombination and parasitic effects in order to identify loss mechanisms and reveal current transport properties in CZTS-based MGL solar cells.
2. Experimental

CZTS monolayers were synthesized from binaries and elemental S in molten flux by isothermal recrystallization process. The details of the monolayer growth technology can be found elsewhere [18]. MGL solar cells with structure: graphite/MGL/CdS/ZnO/glass, were made from powder crystals with a diameter of 56–63 μm as selected by sieving. The analysis area of the solar cell is determined by the back contact area which is typically about 0.04 cm². More details about the solar cell preparation can be found in [19].

For the temperature dependent J–V and EQE measurements solar cells were mounted in a closed cycle He cryostat. J–V measurements were done by decreasing the temperature while EQE measurements were done by increasing the temperature in the range T = 10–300 K.

For EQE measurements the generated photocurrent was detected at 0 V bias voltage. 250 W standard halogen lamp with calibrated intensity (100 mW cm⁻²) was used as a light source and spectrally neutral net filters for intensity dependence.

3. Results and discussion

Room temperature J–V characteristics of a studied CZTS-based MGL solar cell showed the following properties: open-circuit voltage $V_{oc} = 709$ mV, short-circuit current density $J_{sc} = 13.8$ mA/cm², fill factor $FF = 61.4\%$, and efficiency $\eta = 6.0\%$. Due to the peculiarity of the MGL solar cell structure, the active area where the photocurrent is actually produced is smaller than the analysis area. The active area is estimated by isothermal recrystallization process. The details of the solar cell preparation can be found in [19].

Fig. 2. Temperature dependence of dark J–V curves.

The analysis area of the solar cell is determined by the back contact area which is typically about 0.04 cm². More details about the solar cell preparation can be found in [19].

The temperature dependence of the series resistance $R_s$ found using Fig. 2 is shown in Fig. 3a where three different regions can be distinguished.

At temperatures $T > 90$ K (region I), $R_s$ decreases with increasing temperature indicating the thermal activation of carriers [23]. In this region, the $R_s$ can be presented as:

$$R_s = R_{so} \exp(E_A/kT)$$

(2)

where the exponential prefactor $R_{so}$ contains all parameters that are independent or weakly dependent on temperature. Using Eq. (2) the activation energies $E_{A-d} = 87 ± 3$ meV and $E_{A-i} = 43 ± 1$ meV for dark and light curves were found, respectively. These activation energies are in the same range as found in [6,8,24]. At intermediate temperatures ($T = 90–40$ K, region II), the dependence of the series resistance on temperature changes and a typical Mott’s variable-range hopping (VRH) conduction starts to dominate [25]. This type of behavior is expected in all heavily doped materials where spatial potential fluctuations create deep potential wells for holes [6,26,27]. At the same time, we also expect the increasing role of bulk recombination in this temperature region and therefore the VRH model is not completely valid here. At about $T = 40$ K, a rapid change of $R_s$ can be seen. In low temperature region ($T < 40$ K, region III), $R_s$ drops down more than one order of magnitude and remains almost constant down to the lowest measured temperature. At these very low temperatures, generated holes are not able to tunnel through the potential barrier into the interface region between CZTS and CdS and therefore the interface recombination rate must be very low.

Quantum efficiency measurement is a well-known method to describe optical and electronic losses in solar cell devices. From the low-energy side of the EQE curve i.e. near the bandgap energy $E_g$, the effective bandgap energy $E_{g}^\ast$ can be determined [17] by using an approximation proposed by Klenc and Schock [28]:

$$EQE \approx KxL_{d} \approx A\left(E-E_g^\ast\right)^{1/2}/E$$

(3)

where constant $A$ includes all energy independent parameters, $L_{d} = w + L_{d}$ is the effective diffusion length of minority carriers, $L_{d}$ is their diffusion length in the absorber material, $w$ is the width of the depletion region, and $\alpha$ is the absorption coefficient of the absorber material. The constant $K$ is unity in absolute measurements. Consequently, the $E_{g}^\ast$ value can be determined from a plot of

![Fig. 1. Temperature dependence of $V_{oc}$ measured at different light intensities.](image1)

![Fig. 2. Temperature dependence of dark J–V curves.](image2)
temperature to \( T = 180 \, \text{K} \) \( E_g \) follows the model of temperature dependence of the bandgap energy proposed by K.P. O’Donnell and X. Chen [29]. Then \( E_g \) starts to decrease with further decreasing of the temperature until the “critical” temperature at about 40 K where the rapid increase of \( E_g \) starts. Similar behavior can be seen for integrated EQE, see Fig. 3c. It was shown in [17] that the changes at 40 K < \( T < 180 \, \text{K} \) are related to localization of holes inside deep valence band potential wells. As a result, an exponential Urbach tail starts to affect the absorption and the effective bandgap \( E_g \) starts to decrease due to holes localization in deeper potential wells. At the same time the hole mobility also decreases and the bulk recombination through these deep wells increases reducing the overall EQE. The observed sudden increase of \( E_g \) to the “normal” bandgap value \( E_0 \) at 40 K together with the increase of the generated current (EQE) and decrease in \( R_s \) has to be related to the step-like change in the Fermi level position at the interface. This change could cause the blocking of hole transport to the interface states and as a result the interface recombination decreases. This is why the photocurrent and \( E_g \) increase. However, there might be also other processes taking place causing the same kind of behavior. Consequently further studies are needed to explain this peculiar behavior of the CZTS solar cell parameters at very low temperatures.

4. Conclusions

Temperature dependence of CZTS solar cell parameters was measured in the range of \( T = 10–300 \, \text{K} \). It was shown that main recombination losses are related to interface recombination that was found to be blocked at \( T < 40 \, \text{K} \). Part of the losses originate also from bulk recombination and is associated to potential fluctuations of the valence band edge.

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References