Transport properties of $CuGaSe_2$-based thin-film solar cells as a function of absorber composition

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ABSTRACT

The transport properties of thin-film solar cells based on wide-gap $CuGaSe_2$ absorbers have been investigated as a function of the bulk [Ga]/[Cu] ratio ranging from 1.01 to 1.33. We find that (i) the recombination processes in devices prepared from absorbers with a composition close to stoichiometry ([Ga]/[Cu] = 1.01) are strongly tunnelling assisted resulting in low recombination activation energies (E_a) of approx. 0.95 eV in the dark and 1.36 eV under illumination. (ii) With an increasing [Ga]/[Cu] ratio, the transport mechanism changes to be dominated by thermally activated Shockley-Read-Hall recombination with similar E_a values of approx. 1.52–1.57 eV for bulk [Ga]/[Cu] ratios of 1.12–1.33. The dominant recombination processes take place at the interface between CdS buffer and $CuGaSe_2$ absorber independently from the absorber composition. The increase of E_a with the [Ga]/[Cu] ratio correlates with the open circuit voltage and explains the better performance of corresponding solar cells.

1. Introduction

Chalcopyrite $Cu(In_{1-x}Ga_x)(S_ySe_{1-y})_2$ "CIGSSe"-based thin film solar cells are promising candidates for second generation photovoltaic (PV) devices. Respective TCO/buffer/CIGSSe/Mo/glass heterojunction solar cells have already reached power conversion efficiencies as high as 20% on the lab scale [1] and 13.4% on large areas (3459 cm^2) [2]. These high-efficiency PV devices are based on $Cu(In_{1-x}Ga_x)Se_2$ absorbers with a Ga/(In+Ga) = x ratio of approx. 0.25–0.35 [1]. This composition results in absorbers with (bulk) band gap energies (E_g) of approx. 1.1–1.2 eV [1]. An obvious approach to further improve respective device efficiencies is to increase the absorber E_g to approx. 1.35 eV [3] in order to better match the AM1.5 solar spectrum. Another motivation to pursue the development of so called "wide-gap" chalcopyrite solar cells is the quest for monolithically interconnected "all-chalcopyrite"-based tandem solar cell devices. The tandem configuration promises relative efficiency gains of up to 40% [4] compared to single junction devices. Theoretical studies show that an ideal top cell in the tandem configuration should have a band gap of ~1.70 eV [4]. In view of this requirement, $CuGaSe_2$ thin films with a bulk band gap of 1.68 eV [5] are regarded as suitable absorbers for the top cell of tandem PV devices. However, single junction solar cells based on "wide-gap" chalcopyrites tend to fall behind with respect to their performances compared to those based on "low-gap" chalcopyrites. One explanation for this observation is the deviation from the expected linear behaviour of the V_{oc} as a function of E_g for absorbers with band gaps higher than 1.25 eV [6]. Hence, current record solar cells prepared from $CuGaSe_2$ single crystals only yield efficiencies of 9.7% with an open circuit voltage (V_{oc}) of 946 mV [7], while thin film PV devices achieve efficiencies of 9.5% with an V_{oc} = 905 mV [8]. In our lab, efficiencies of 8.7% have been achieved by using $CuGaSe_2$ thin films deposited by chemical close-spaced vapor transport (CCSVT) [5,9].

In order to address this issue, we have investigated the transport properties of thin film n^+-ZnO/i-ZnO/CdS/$CuGaSe_2$/Mo/glass solar cells as a function of the $CuGaSe_2$ bulk [Ga]/[Cu] composition. The device transport properties have been investigated by illumination- and temperature-dependent current–voltage [J(V,T)] measurements. We find that independent from the absorber composition the dominant recombination process takes place at the interface between CdS buffer and $CuGaSe_2$ absorber. However, the transport mechanism in devices prepared from $CuGaSe_2$ thin films close to stoichiometry is dominated by strong tunnelling processes, while the use of Ga-rich absorbers results in predominant thermally assisted Shockley-Read-Hall recombination processes. Furthermore, we find a good correlation between the obtained activation energies (E_a) of charge carrier recombination and the open circuit voltages (V_{oc}) of corresponding devices.

2. Experimental details

For the preparation of solar cells, $CuGaSe_2$ thin film absorbers with bulk [Ga]/[Cu] ratios between 1.01 and 1.33 (±0.03) were grown by the CCSVT technique [9] onto Mo covered soda-lime glass (SLG) substrates. The films are prepared in two stages via chemical reactions between the Cu precursor and $GaCl_x/H_2Se$ vapors. Annealing steps in pure H_2 atmosphere are used between the two growth stages as well as at the end of the second growth stage. All the films in the compositional range investigated are polycrystalline with triangular-like grain shapes and sizes of up to 2 μm. Although the films surface is kept under Ga-rich conditions during the applied growth stages, the observed morphology is typical of layers grown under Cu-rich conditions ensured by the usage of the Cu precursor. The elements depth profiling of the prepared films shows a homogeneous distribution of Cu, Ga and Se in the absorber bulk independently on composition [10]. The photoluminescence (PL) studies show additionally a homogeneous distribution of the intrinsic defects in stoichiometric absorbers as well as in samples with $[Ga]/[Cu] \geq 1.24$ [10]. Only slight defect gradients from the films back- to the topside are observed. The concentration of the deep defect levels associated with Ga vacancies decreases with the increase of the integral bulk Ga content. Simultaneously, PL measurements reveal a broadening as well as a shift to lower energies of the D1A1 emission line (with a peak position at 1.67 eV for stoichiometric samples) related to shallow donor-to-acceptor pair recombination. The latter effect is described within the model of potential fluctuations. X-ray photoelectron spectroscopy studies showed no presence of secondary phases, e.g. $Cu_{2-x}Se$, in any of investigated samples [11]. The films surface composition changes from being slightly Cu-poor and slightly Ga-rich for the $CuGaSe_2$ sample with a bulk [Ga]/[Cu] ratio of 1.01 to being close to the $CuGa_3Se_5$ composition for the sample with a bulk [Ga]/[Cu] ratio of 1.33.

Solar cell devices consisting of ZnO:Ga/i-ZnO/CdS/$CuGaSe_2$/Mo/SLG structures were processed from as-grown $CuGaSe_2$ films. A 50-nm-thick CdS buffer layer was prepared by chemical bath deposition (CBD) at 60 °C. The sputtered window layer consists of a 90 nm intrinsic and a 400 nm highly Ga-doped n^+-type ZnO. Ni/Al grids were e-beam evaporated to provide the front contacts.

The bulk [Ga]/[Cu] ratio of the prepared $CuGaSe_2$ thin films on Mo/SLG substrates was determined by means of well calibrated X-ray fluorescence analysis (XRF) using a Philips MagiXPro PW2400 spectrometer.

The illumination dependent J(V,T) measurements were performed in an evacuated N_2-cooled cryostat using a Keithley source measure unit in four-point configuration. The samples were illuminated by an ELH-type halogen lamp with a maximum illumination adjusted to 100 mW/cm^2. A set of neutral density filters served for adjusting the light intensity between 0.05 and 100 mW/cm^2.

3. Results and discussion

The transport mechanism in $CuGaSe_2$-based solar cells in the dark was investigated by analysing the data extracted from the dark J(V,T) measurements. Since the superposition principle is not valid under illumination because of the voltage-dependent photocurrent in chalcopyrite solar cells [12], the illuminated J(V) curves are not suitable for analysis. Instead, the short-circuit current density (J_{sc}) vs. V_{oc} curves were used for the determination of the diode ideality factors (A) under illumination and the saturation current densities (J_0). Based on that data the corresponding recombination activation energies under illumination were determined. Additionally, the recombination activation energies under illumination were extracted from $V_{oc} = f(T)$ curves. The corresponding evaluations were performed according to the one-diode model adapted for chalcopyrite solar cells [13].

The dark J(V) and $J_{sc} - V_{oc}$ characteristics could be well fitted with a one-diode equation by taking into account the series resistance (R_s), and the parallel resistance (R_p):

$$J = J_0\left[exp\left(\frac{q(V-JR_S)}{AkT}\right)-1\right] + \frac{V-JR_S}{R_P} - J_{SC}, \tag{1}$$

where q and k are the elementary charge and Boltzmann-constant, respectively. According to Ref. 10, the diode saturation current can be expressed by:

$$J_0 = J_{00}\, exp\left(\frac{-E_a}{AkT}\right), \tag{2}$$

where J_{00} is a weakly temperature-dependent prefactor. By reorganising Eq. (2) to the relationship

$$A\, ln(J_0) = -\frac{E_a}{kT} + A\, ln(J_{00}), \tag{3}$$

a refined evaluation of E_a is attained. Thus, a plot of the corrected saturation current density $A \times ln(J_0)$ versus the inverse temperature 1/T should yield a straight line with a slope corresponding to E_a. This method for the determination of E_a is applied for both, dark and illuminated measurements. Additionally, the illuminated E_a values could be determined from $V_{oc} = f(T)$ curves. Considering in Eq. (1) the high parallel resistance and neglecting the series resistance of illuminated solar cell devices, the open circuit voltage can be expressed by

$$V_{oc} = \frac{E_a}{q} - \frac{AkT}{q}\, ln\left(\frac{J_{00}}{J_{sc}}\right). \tag{4}$$

By extrapolating the $V_{oc} = f(T)$ curves to T = 0 °K, the activation energy under illumination can be determined. If $E_a = E_g$ ($E_a < E_g$) the dominant recombination process is located in the absorber bulk (at the buffer/absorber interface).

The forward dark $J(V,T)$ curves and the $J_{sc} - V_{oc}(T)$ plots of the investigated solar cell devices show similar behaviour in the region of lower voltages and some differences at higher ones (not shown; an example can be found in Ref.5). The $J_{sc} - V_{oc}$ plots exhibit an exponential dependence over more than two orders of magnitude between 180° and 320 °K, which makes this temperature range suitable for the current transport analysis. Note that the limitation by the devices' R_s is not reached in the $J_{sc} - V_{oc}$ characteristics.

The temperature dependence of the diode quality factors of illuminated $CuGaSe_2$-based solar cells with absorbers of different [Ga]/[Cu] composition is presented in Fig. 1. Values below two are observed in the high temperature region on all the investigated devices. However, the A values of the device with a $CuGaSe_2$ bulk [Ga]/[Cu] ratio of 1.01 (i.e., an absorber composition which is close to stoichiometry — "stoichiometric absorber"), show a strong temperature-dependent behavior. The respective values change between 1.8 at 300 °K and 3.6 at 180 °K. This indicates a strong contribution of

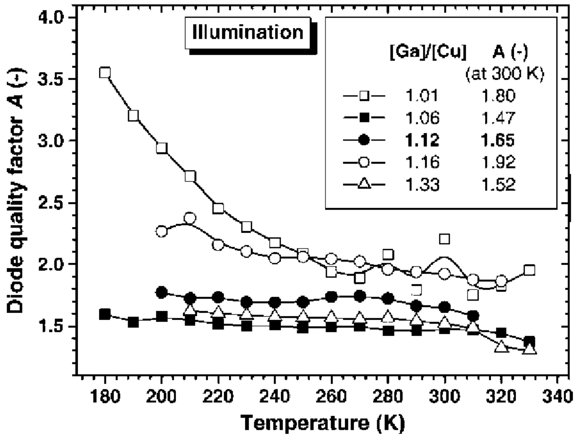

Fig. 1. Temperature dependence of the diode quality factors, A, of $CuGaSe_2$-based solar cell devices prepared from absorbers with different [Ga]/[Cu] bulk ratios as extracted from $J_{sc} - V_{oc}$ plots. The insets show the corresponding A values determined at 300 °K.

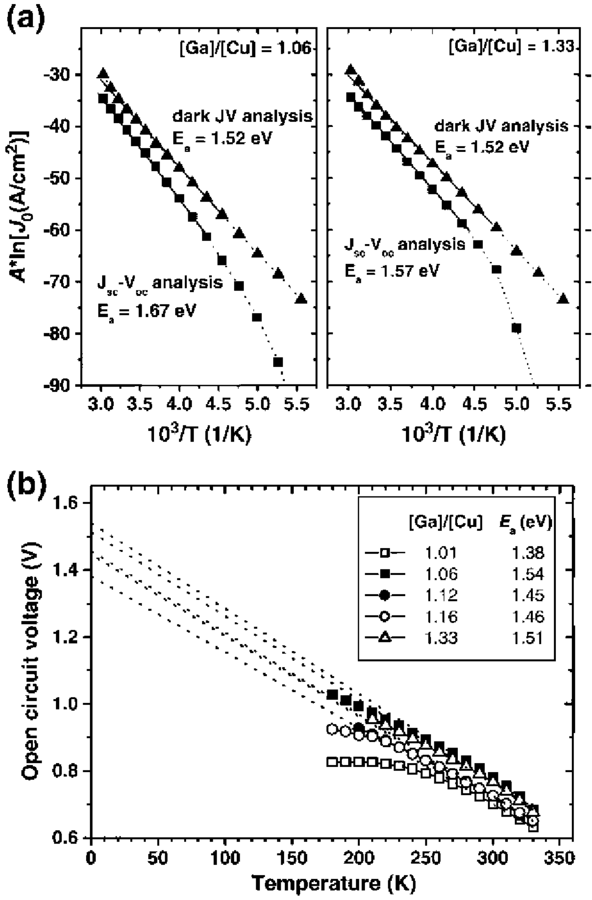

Fig. 2. (a) Arrhenius plot of the diode quality factor corrected saturation current density, J_0, of CuGaSe$_2$-based solar cells prepared from absorbers with different [Ga]/[Cu] bulk composition. The activation energies, E$_a$, of recombination processes in the dark and under illumination were extracted by fitting the respective $A \times \ln J_0$ curves to Eq. (2). The solid lines show the corresponding fits. (b) Open circuit voltage as a function of temperature of respective devices. The dotted lines show the fits to Eq. (4). The insets show the corresponding activation energies under illumination.

tunnelling effects to the dominant recombination process. Some fluctuations of the *A* values observed on samples of stoichiometric absorbers could be explained by the charging-discharging effects related presumably to deep levels caused by Ga-vacancies which have a higher concentration in these absorber films [10] (see the experimental chapter). Most of the devices based on absorbers with [Ga]/[Cu] ratios higher than 1.06, however, show temperature-independent values between 1.5 and 1.7 in a large temperature range of 200–310 °K. Thus, it could be concluded that the recombination of charge carriers in these solar cells occur via deep levels. In summary, in devices based on stoichiometric absorbers the transport mechanism is dominated by tunnelling enhanced processes, while in devices from Ga-rich absorbers the recombination mechanism is thermally assisted in a large temperature region. Moreover, the temperature independence of *A* for the latter devices indicates that the recombination occurs via a single dominant recombination center, which is described by the Shockley–Read–Hall recombination model [14]. Note that the reported thermally activated process in such a large temperature region is specifically observed on solar cell devices prepared from CCSVT-deposited CuGaSe$_2$ thin films [5]. So far, tunnelling enhanced recombination has always been reported as being the dominant process for CuGaSe$_2$-based solar cells with absorbers deposited by physical vapour deposition [13,15]. Thus, it could be concluded that the absorber bulk properties as well as the chemical and electronic structure of the buffer/absorber interface are influenced by the absorber preparation details.

In the dark the temperature dependence of the diode ideality factors is more pronounced (not shown). *A* takes overall higher values: The devices with [Ga]/[Cu] ratios of 1.01 and 1.06 show *A* values over 4.0 at low temperatures (below 220 °K). At higher temperatures, values between 1.8 and 2.0 are recorded. However, compared to illuminated devices the range of the diode ideality factor temperature independence is significantly reduced, e.g., extending only between 260 and 320 °K. Correspondingly, the application of the Shockley–Read–Hall recombination model becomes restricted to the latter temperature range.

The activation energy of charge carrier recombination in the investigated devices is determined from the modified Arrhenius *A*ln (J_0) vs. 1/*T* graphs, as exemplary presented in Fig. 2(a) for two devices based on absorber with different bulk [Ga]/[Cu] ratios. In the dark, the slopes of the Arrhenius plots depend on the absorber bulk [Ga]/[Cu] ratio, resulting in different activation energies: 0.95, 1.67 and 1.52–1.57 eV for the [Ga]/[Cu] ratios of 1.01, 1.06 and 1.12–1.33, respectively. Under illumination, the slopes of the Arrhenius plots (based on *A* and J_0 data extracted from $J_{sc} - V_{oc}$ curves) yield activation energies between 1.36 and 1.52 eV. Thus, the recorded recombination energies ranging from 0.95 to 1.67 eV are lower than the CuGaSe$_2$ bulk band gap of 1.68 eV [5]. This suggests that the dominant recombination mechanism is located at the buffer/absorber interface. Although for the device with an absorber [Ga]/[Cu] composition of 1.06 an E$_a$ value of 1.67 eV close to the CuGaSe$_2$ bulk band gap is found in the dark, we do not expect the device to be limited by bulk but rather by interface recombination. Reason for that conclusion gives the finding of an enlarged band gap at the surface of CuGaSe$_2$ absorbers [16]. Together with an expected negative conduction band offset [5,11], this supports that the dominant recombination mechanism for all CuGaSe$_2$-based solar cell devices (independent of absorber bulk composition) is located at the CdS/CuGaSe$_2$ interface. This finding is in agreement with early theoretical [17] and experimental [18] works which stated that a cliff-like conduction band offset limits the open circuit voltage due to an increased interface recombination [19]. In addition, the interface recombination is expected in CuGaSe$_2$ solar cells due to the lack of an inverted conductivity type at the absorber/buffer interface [13].

The recombination activation energies for devices under illumination were again independently determined from the V$_{oc}$ = f(T) data in Fig. 2(b). All the determined E$_a$ values (presented in the inset to Fig. 2(b)) agree well with the values determined from *A*ln(J_0) vs. 1/*T* graphs. This agreement is illustrated in Fig. 3, where the dark E$_a$ values are additionally presented. It can be observed that devices from stoichiometric absorbers ([Ga]/[Cu] = 1.01) show the lowest recombination activation energies as well as the largest difference between the corresponding values in the dark (E$_a$ = 0.95 eV) and under

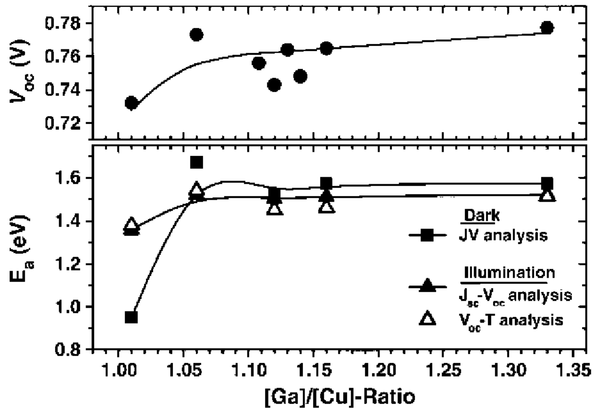

Fig. 3. The activation energy, E$_a$, in the dark and under illumination, and the open circuit voltage, V$_{oc}$, of the CuGaSe$_2$-based solar cell devices as a function of the absorber bulk [Ga]/[Cu] ratio. The lines are guides to the eye.

illumination ($E_a = 1.36$ eV). This difference decreases with increasing [Ga]/[Cu] ratio resulting in similar values from a [Ga]/[Cu] ratio of around 1.12. The E_a values (under illumination) monotonically increase from 1.36 eV for [Ga]/[Cu] = 1.01 to 1.55 eV for [Ga]/[Cu] = 1.33. The observed E_a behaviour is very similar to that of the devices' open circuit voltages (see Fig. 3), which might be the indication for a $E_a - V_{oc}$ correlation. If this conclusion is correct, then the increase of E_a with increasing [Ga]/[Cu] ratio also explains the improvement of the photovoltaic performances of corresponding solar cells, which show a pronounced increase in the power conversion efficiency with an increase in the [Ga]/[Cu] bulk ratio (reaching a maximum of 8.7% for [Ga]/[Cu] = 1.12) [5]. The slight decrease of solar cell PV parameters at higher [Ga]/[Cu] ratios (of approx. 1.33) could be explained by the effects of high doping and compensation (in highly Ga-rich $CuGaSe_2$ films) on the absorber band structure described by the model of fluctuating potentials [10,20].

4. Conclusions

We have investigated the transport properties of $CuGaSe_2$-based thin-film solar cells as a function of the $CuGaSe_2$ bulk [Ga]/[Cu] composition ($1.01 \leq [Ga]/[Cu] \leq 1.33$). We find that the dominant recombination mechanism is located at the buffer/absorber interface, independent of absorber composition. However, the recombination in devices prepared from $CuGaSe_2$ absorbers with a near-stoichiometric composition is enhanced by tunnelling effects. Thermally activated Shockley–Read–Hall recombination processes become predominant in devices based on absorbers with a bulk [Ga]/[Cu] ratio higher than 1.12. The latter mechanism applies especially for illuminated devices. The found behaviour of the activation energy with the absorber composition correlates well with the behaviour of the devices' open circuit voltages. The monotonic increase of E_a with increasing [Ga]/[Cu] ratio also explains the overall improvement of the corresponding solar cell PV parameters.

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