Effects of irradiation of ZnO/CdS/Cu$_2$ZnSnSe$_4$/Mo/glass solar cells by 10 MeV electrons on photoluminescence spectra

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A B S T R A C T

Solar cells with the structure ZnO/CdS/Cu$_2$ZnSnSe$_4$/Mo/glass were studied by photoluminescence (PL) before and after irradiation with a dose of 1.8×10^{15} cm^{-2} and then 5.4×10^{15} cm^{-2} of 10 MeV electrons carried out at 77 K in liquid nitrogen bath. The low temperature PL spectra before irradiation revealed two bands, a broad and asymmetrical dominant band at 0.94 eV from the CZTSe layer and a lower intensity high energy band (HEB) at 1.3 eV, generated by defects in the CdS buffer layer. Analysis of the excitation intensity and temperature dependencies suggested that the dominant band is free-to-bound (FB): the recombination of free electrons with holes localised at acceptors whose energy levels are affected by potential fluctuations of the valence band due to high concentrations of randomly distributed charged defects. Irradiation did not induce any new band in the examined spectral range (from 0.5 μm to 1.65 μm) but reduced the intensity of both bands in the PL spectra measured at 77 K without warming the cells. The higher the dose the greater was the reduction. After this the cells were warmed to 300 K and moved to a variable temperature cryostat to measure temperature dependencies of the PL spectra. After irradiation the red shift rate of the FB band with temperature rise was found to increase. Electrons displace atoms in the lattice creating primary defects: interstitials and vacancies. These defects recombine during and shortly after irradiation forming secondary defect complexes which work as deep non-radiative traps of charge carriers reducing the PL intensity and increasing the rate of the temperature red shift. Irradiation did not affect the mean depth of the band tails estimated from the shape of the low energy side of the dominant PL band.

1. Introduction

The semiconductor compound Cu$_2$ZnSnSe$_4$ (CZTSe) is used in the absorber layer of thin film solar cells. A bandgap of 1 eV, high absorption coefficient [1] in the region of the solar spectrum along with high known reserves of the chemical elements, constituting this compound, their relatively low costs and toxicity make this semiconductor very attractive for sustainable photovoltaics (PV) whereas a record conversion efficiency of 11.6% [2] for laboratory size devices places such cells amongst leaders of sustainable thin film PV [3].

The lattice structure of Cu$_2$ZnSnSe$_4$ can be built by the substitution of In/Ga in Cu(InGa)Se$_2$ (CIGS) with alternating Zn and Sn [4]. Such a substitution transforms the chalcopyrite structure of CIGS to a kesterite one of CZTSe. A great advantage of CZTSe is the significant similarity of its structural and electronic properties with those of CIGS [5]. This similarity greatly helps to understand such properties and accelerates

the process of development of CZTSe-based electronic devices. One of the key features of CIGS compared to other semiconductor materials for solar cells is an outstanding radiation hardness of the material itself and CIGS-based solar cells. High doses of MeV electrons already detrimental for Si- and GaAs-based solar cells do not change the principal parameters of CIGS-based devices [6]. The tolerance of CIGS solar cells to MeV protons is also remarkable. It exceeds that of Si-based devices by a factor of 50 [7]. The recently reported comparison of such a tolerance of CZTSe- and CIGS-based solar cells demonstrates that CZTSe-based devices are more tolerant to MeV protons that the CIGS ones [8]. Such an extraordinary radiation hardness demonstrates a great potential for the use of such devices in spacecraft power generators.

The investigation of the influence of irradiation on the photoluminescence (PL) spectra is of a great importance because PL is a powerful tool for studying the electronic and optical properties of semiconductors. Changes in the PL spectra can reflect modifications in

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the defect content generated by irradiation. Such modifications may lead to an improvement or degradation of solar cell performance. Electronic defects determine the doping level as well as the recombination centers of a solar cell absorber. The effect of keV Ar$^+$ ion-beam dry etch on the PL spectra of CZTSe thin films has recently been reported [9]. The tolerance of CZTSe-based solar cells to high energy electrons was examined earlier [10], but nevertheless further investigation of the influence of electron beam irradiation on PL spectra and especially on the temperature dependence of the PL spectra is needed to clarify the nature of the defects generated by such an irradiation. Studies of the effect of irradiation on solar cell electric parameters demonstrate the integrated effect of irradiation on all layers of the cell whereas examination of the PL spectra measured before and after irradiation provides an opportunity to separately analyse changes in the absorber layer and in the buffer layer of CdS.

In this paper we study the effect of 10 MeV electron irradiation on the PL spectra of CZTSe solar cells and analyse the nature of defects generated by these electrons.

2. Experimental details

Solar cells with the structure ZnO/CdS/Cu$_2$ZnSnSe$_4$/Mo/glass were fabricated at Northumbria University. Multilayer metallic precursors, containing several nanometers thick alternating Cu, Zn and Sn layers, were sequentially deposited on Mo/glass substrates (mounted on a rotating table) by three-target magnetron sputtering of high-purity (5 N) Cu, Zn and Sn targets at room temperature. The CdS buffer layer was grown using a standard chemical bath deposition (CBD) process at 70 °C after etching the films with a 10 wt% KCN solution for 30 s. Solar cells with an area of 3 × 3 mm^2 were then fabricated by DC-magnetron deposition of ZnO/ZnO:Al transparent front contacts and mechanical scribing. More information on the fabrication process of the films can be found elsewhere [11–14].

The elemental composition of the CZTSe film was measured using a combination of energy dispersive x-ray (EDX) and x-ray fluorescence (XRF) techniques is shown in Table 1.

A detailed characterization of the CZTSe films such as their structural properties, the presence of secondary phases, studied using room temperature Raman scattering and X-ray diffraction (XRD), as well as principal parameters of the solar cell (the open circuit voltage V$_{oc}$, short circuit current I$_{sc}$, fill factor F and conversion efficiency η) fabricated from these films have also been reported earlier [11,13,14].

Two-stage irradiation of these solar cells was carried out by 10 MeV electrons at a current density of 10^{13} cm^{-2}·s^{-1} at 77 K in liquid nitrogen bath. During the first stage the cells were irradiated with a dose of 1.8 × 10^{15} cm^{-2} whereas during the second stage the dose was increased to 5.4 × 10^{15} cm^{-2}.

The influence of such irradiation on the optical and electronic properties of the CZTSe layer was studied by PL. Measurements of the effect of excitation intensity change of the PL spectra were carried out at 77 K in a liquid nitrogen cryostat straight after irradiation without raising the sample temperature. Then the samples were warmed up to the room temperature, transferred to a variable temperature closed-cycle helium cryostat where temperature (varying from 8 K to 350 K)

Table 1
The [Cu]/[Zn + Sn] and [Zn]/[Sn] ratios in the film and parameters of solar cell fabricated from it [14].

[Cu]/[Zn + Sn] - EDX	0.75
[Zn]/[Sn] - EDX	1.17
[Cu]/[Zn + Sn] - XRF	0.80
[Zn]/[Sn] - XRF	1.18
V$_{OC}$ (mV)	410
J$_{SC}$ (mA/cm2)	31.9
FF	56.3
η (%)	7.4

dependencies of the spectra were examined using a single grating monochromator MDR-23 with a focal base of 60 cm and a 600 groves/mm diffraction grating. PL emission was excited by the 532 nm line of a laser. The dispersed PL signal was detected by a cooled Hamamatsu InGaAs p-i-n-photodiode, sensitive from 0.5 µm to 1.65 µm. A lock-in amplifier along with a laser beam chopper were used to reduce the noise level.

3. Results and discussion

At low temperatures the PL spectra of the solar cell before irradiation include a broad, high intensity dominant band at 0.94 eV red shifting at increasing temperature. A temperature dependence of the PL spectra of the cell before irradiation is presented in Fig. 1(a) on a logarithmic scale.

We assign the dominant band to a free-to-bound (FB) transition: recombination of free electrons from the conduction band with holes localised at an acceptor whose energy level is spread by potential fluctuations. The recombination model describing such types of transition was developed in Ref. [15] and applied to interpret PL spectra of Cu (InGa)Se$_2$ [16] and CZTSe [11,12,17]. The spectrum also reveals a broad and low intensity high energy band (HEB) at 1.35 eV which was earlier assigned to defects in the CdS layer [17]. At higher temperatures the FB band quenches revealing a band-to-band (BB) recombination of free electrons with free holes. PL measurements were performed in liquid nitrogen bath before and straight after irradiation without warming the samples to the room temperature. Fig. 1(b) shows changes in the FB band (measured at 77 K) caused by irradiation. It can be seen that the spectral position and shape of FB do not change. The first dose of irradiation at 77 K (1.8 × 10^{15} cm^{-2}) reduces the intensity of FB by a factor of 1.3. The second dose (5.4 × 10^{15} cm^{-2}) reduces it further by a factor of 1.4. The excitation intensity dependence of the PL spectra, measured before and after irradiation, demonstrated a significant blue shift of the FB band with a j-shift of 20 meV per decade of the laser intensity change and a coefficient k, measured as the gradient of the dependence of the PL intensity on the laser excitation power plotted on a log-scale, of 1.0. The dependence of the FB band PL intensity on the excitation laser power, measured before and after irradiation, is presented in Fig. 1 (c). Both j and k remain unchanged by irradiation.
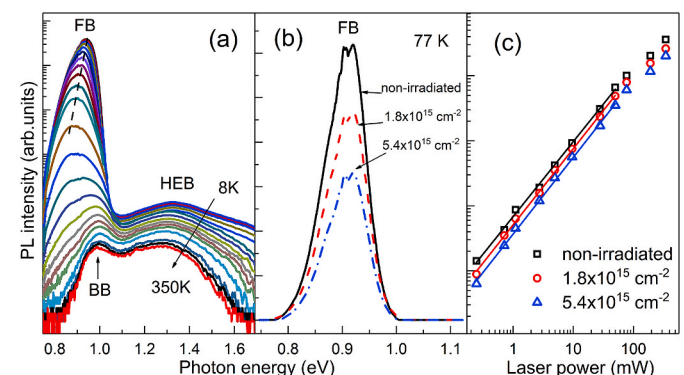
After irradiation and the measurements in liquid nitrogen the solar cells were warmed up to the room temperature, transferred to a variable temperature closed-cycle helium cryostat, where temperature dependencies of the PL spectra were measured. The PL spectra measured at 8 K before and after irradiation are presented at Fig. 2 on a linear (a) and logarithmic scale (b).

Similar to the measurements in liquid nitrogen, the intensity of the FB band at 8 K decreased after each irradiation. Irradiation also


Fig. 1. Temperature dependence of PL spectra for non-irradiated solar cell (a), PL spectra of the solar cell measured at liquid nitrogen temperature before and after irradiation with a dose of 1.8 × 10^{15} cm^{-2} and 5.4 × 10^{15} cm^{-2} using similar optical alignments and laser excitation on a linear intensity scale (b), the dependence of the PL intensity of the FB band on the excitation laser power (c).
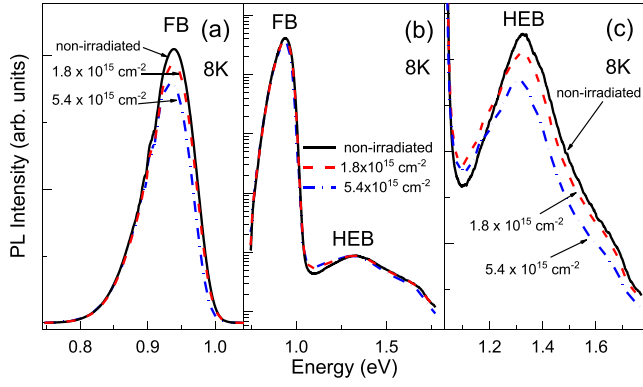
Fig. 2. The PL spectra measured at 8 K before and after irradiation on a linear (a) and logarithmic scale (b), and the HEB PL band (c).

decreases the intensity of the HEB band as shown in Fig. 2(c). Small red shifts of a few meV for both the FB and HEB peaks after irradiation was also observed. These shifts can be due to inhomogeneity of the sample or small changes in the optical alignment.

In order to improve the accuracy of analysis of the dominant FB band dependence on the excitation intensity and temperature, and to be able to subtract the BB and the HEB bands it is essential to have an accurate description of the PL bands shape. This is provided by fitting the experimental spectra with the empirical asymmetric double sigmoid function (DSF) proposed in Refs. [16]:

$$I(h\nu) = A\left\{1 + exp\left[-\frac{(h\nu - E_1)}{W_1}\right]\right\}^{-1} * \left\{1 - \left(1 + exp\left[-\frac{(h\nu - E_2)}{W_2}\right]\right)^{-1}\right\},$$

$$(1)$$

where A, E_1, E_2, W_1 and W_2 are the experimental parameters. Parameters E_1 and W_1 represent the shape of the low-energy side of the PL bands while E_2 and W_2 belong to the high-energy side. According to Ref. [16] W_1 specifies the average depth of potential fluctuations $\gamma = 22$ meV.

The DSF fitted in the PL spectra measured before irradiation at temperatures of 8 K and 210 K are shown at Fig. 3 (a) and (b), respectively. The intensity of the FB band decreases with temperature rising and the shape of this band also changes. The temperature dependence of the W_1 and W_2 fitting parameters is presented in Fig. 3 (c). Increasing temperature does not change much W_1 whereas W_2 increases as $W_2 \sim 2$ kT [16] and at T = 110 K both parameters become almost equal making the shape of FB more symmetrical. It can be seen that the shape of the FB
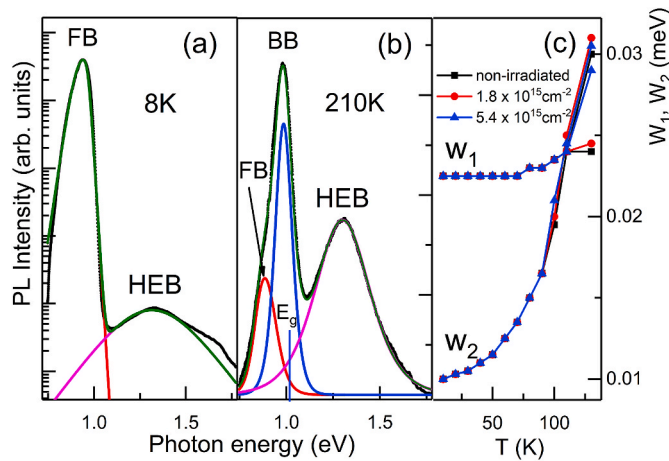
band changes very little after irradiation. At temperatures above 150 K the HEB band is apparent and becomes dominant in terms of peak intensity at 210 K as it is seen in Fig. 3 (b).

At room temperature the FB band quenches completely whereas the BB band is still visible although its intensity decreases after irradiation as shown in Fig. 4 (a). Before the irradiation the spectral energy of the FB band maximum $E_{max}(T)$ red shifts with rising temperature as shown in Fig. 4(b). Irradiation results in a steeper fall of $E_{max}(T)$ with the temperature increase. The higher the dose the steeper is the fall. A similar influence on $E_{max}(T)$ induces a decrease of the laser excitation power as it can be seen in Fig. 4(c). According to Ref. [15] $E_{max}(T)$ depends on the concentration of free charge carriers, electrons (n) and holes (p) as follows:

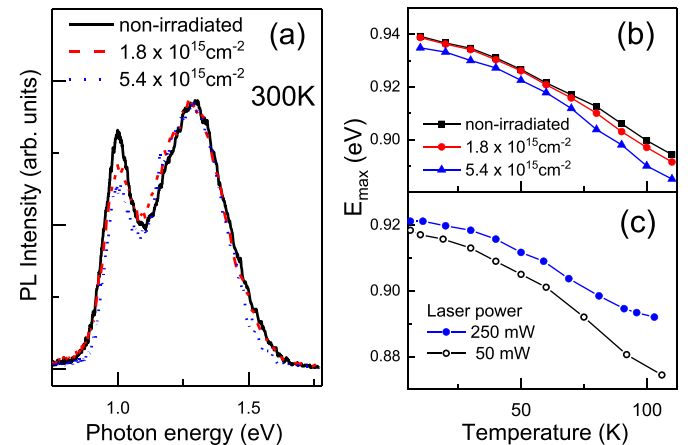$$E_{max}(T) = E_{max}(6K) - kT \ln[N_v / (p + \theta n)], \qquad (2)$$

where N_v is the valence band effective density of states and θ is the ratio of probabilities for an electron to that for a hole to be captured at the localised state. In this formula we do not take into account the bandgap dependence on temperature because we are interested in the difference in the red shift rate before and after irradiation. Lower laser excitation intensities result in lower carrier concentrations leading to a steeper temperature dependence of $E_{max}(T)$. We propose that the same effect is observed after electron irradiation. An increase in the concentration of deep traps, generated by irradiation, also makes $E_{max}(T)$ steeper as shown in Fig. 4(b).

Deep non-radiative defects formed by irradiation act as traps of charge carriers reducing their concentration and mobility which lead to a deeper red shift of the dominant PL band. The higher the dose the greater is the degree of the change. A decrease in the carrier concentration after the electron irradiation was observed earlier for CuInSe$_2$ [18].

Before irradiation increasing temperature quenched the intensity of the FB band. Irradiation increased the rate of such quenching as shown in Fig. 5(a). We assign this effect to an increase in the concentration of non-radiative traps generated by irradiation. Arrhenius analysis of the FB band temperature quenching was carried out by calculating integrated PL intensities under the FB shape. Arrhenius plots of these dependencies before and after irradiation are shown in Fig. 5 (b), (c), (d). The best fits were achieved for a single recombination channel [19]:

$$I(T) = I_0/[1 + A_1 T^{3/2} + A_2 T^{3/2} \exp(-E_a/k_B T)], \qquad (3)$$

where I_0 is the dominant band integrated intensity at the lowest temperature of 8 K, A1 and A2 are process rate parameters. The activation

Fig. 3. Experimental PL spectra (symbols) measured at 8 K (a) and 210 K (b), fitted with DSFs (solid lines), the temperature dependence of the W1 and W2 fitting parameters (c).

Fig. 4. PL spectra of the cells measured at 300 K before and after irradiation (a). Temperature dependence of the spectral position of the FB band (E_{max}) before and after irradiation with doses of 1.8×10^{15} cm^{-2} and 5.4×10^{15} cm^{-2} (b), temperature dependence of E_{max} measured at two different excitation laser powers (c).
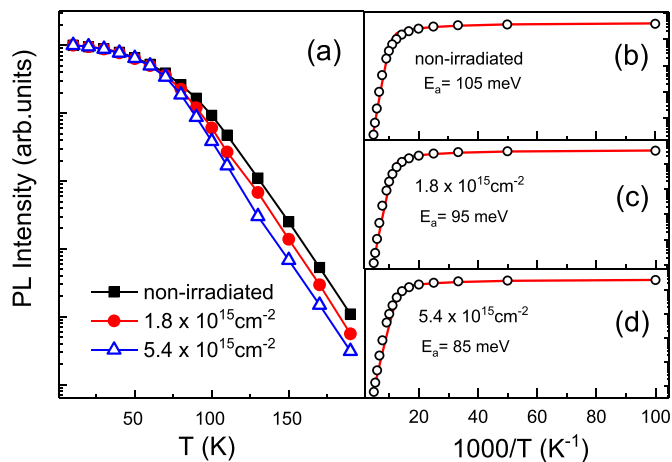
Fig. 5. Dependence of the normalised intensity of FB on temperature before and after irradiation with doses of 1.8×10^{15} cm^{-2} and 5.4×10^{15} cm^{-2} (a). Arrhenius plots of the intensity of FB before (b) and after irradiation with doses of 1.8×10^{15} cm^{-2} (c) and 5.4×10^{15} cm^{-2} (d).

energy E_a was determined to be 105 meV, 95 meV and 85 meV for the PL spectra before irradiation, after the doses of 1.8×10^{15} cm^{-2} and 5.4×10^{15} cm^{-2}, respectively, gradually decreases with rising doses.

Electrons collide with atoms of the CZTSe lattice and displace them forming primary structural defects, vacancies and interstitial atoms of Cu, Zn, Sn, and Se. Due to their high energy these electrons create homogeneous concentrations of defects in the whole volume of the CZTSe and CdS layers.

In Ref. [20] single crystals of CuInSe$_2$ were irradiated with 2 MeV electrons at 4.2 K. The irradiated samples were transferred in liquid nitrogen to a cryostat and studied by positron lifetime spectroscopy at temperatures from 90 K to 580 K. A comparison of the positron lifetime, measured at 90 K, with theoretical values demonstrated the appearance after irradiation of di-vacancy type defects suggesting that mono-vacancies, generated in collision processes by electrons, are mobile at low temperatures. On the other hand interstitial atoms are known to be mobile at low temperatures in binary semiconductors. In ZnSe, which is a binary analogue of CuInSe$_2$, interstitial atoms are mobile at temperatures as low as 1.5 K [21]. Therefore, it might be reasonable to assume that in CZTSe primary defects are also mobile at 77 K. They recombine during and shortly after irradiation forming more stable secondary defect complexes. This is supported by our discovery that irradiation did not induce any new band in the PL spectra (within the examined spectral range) and after warming the samples up to the room temperature the shape of these spectra also did not change.

Therefore the observed reduction in the intensity of the PL bands after irradiation can be explained by the formation of secondary defects acting as deep non-radiative traps of charge carriers reducing their concentration which is supported by the increase in the redshift rate of the FB band caused by rising temperature. The resulting secondary defects may also emit PL radiation at wavelengths beyond the limitation of our detector of 1.65 μm. Irradiation with MeV electrons, carried out at low temperatures, induces new bands in the PL spectra of such binary semiconductors as ZnSe [21], ZnO [22] and GaN [23]. MeV electrons also induce new bands in the PL spectra of CuInSe$_2$ [24] and Cu(In,Ga) Se$_2$ [25].

A reduction of the PL intensity and redshift of the dominant PL band were also observed after irradiation of CuInSe$_2$ by H$^+$ ions [26]. But such irradiation also led to some changes in the shape of the low-energy side of the PL band at low temperatures suggesting an increase of the mean depth of potential fluctuations. Probably, hydrogen becomes chemically bonded in the secondary defects making them less mobile. Similar changes in the PL spectra of the CZTSe thin films were observed after ion beam etching by Ar$^+$ ions [9]. Nevertheless, in the case of electron

irradiation the mean depth of potential fluctuations was not changed. This difference might be because electrons in contrast to hydrogen and argon ions create simpler secondary defects which do not increase the depth of the band tails.

Due to the zinc excess and copper deficiency elemental composition we suggest that in the irradiated CZTSe layers we can expect high concentrations of Zn$_{Cu}$, Cu$_{Zn}$, whose formation energies in CZTSe are very low, and their neutral defect complexes with the acceptor V$_{Cu}$: Cu$_{Zn}$ + V$_{Cu}$ [27].

4. Conclusion

We studied the effect of irradiation of CZTSe solar cells by 10 MeV electrons at 77 K on the PL spectra. Before irradiation the low temperature spectra revealed a high intensity dominant band FB at 0.94 eV, assigned to the recombination of free electrons with holes localised at acceptors with energy levels spread by potential fluctuations of the valence band, and a broad low intensity band HEB at 1.3 eV, attributed to defects in the CdS layer. Within the examined spectral range irradiation did not induce any new bands. However it reduced the intensity of both bands. The higher the dose the greater was the degree of such reduction whereas the shape of FB remained the same suggesting that the mean depth of potential fluctuations was not affected by irradiation. These can be explained by the formation of secondary defect complexes, generated by irradiation, working as deep non-radiative traps and causing a reduction in the concentration of charged carriers. This is supported by an increase in the red shift rate of the FB band found after irradiation at rising temperature.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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