Irradiation of Cu(In, Ga)Se$_2$ Thin Films by 10 MeV Electrons at 77 K: Effect on Photoluminescence Spectra

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Thin films of Cu(In, Ga)Se$_2$ on Mo/glass were irradiated by 10 MeV electrons at 77 K and examined by photoluminescence at 77 K before and after irradiation without warming the samples as well as after warming to 300 K. The photoluminescence spectra revealed a broad band constituting 3 merged peaks (P1, P2, P3) assigned to: band-to-band recombination (P1) and recombination of free electrons with holes localised at acceptors influenced by the valence band tail (P2, P3). Irradiation reduced the intensity of the peaks due to deep traps generated by electrons and anomalously reduced the degree of compensation of the material.

Keywords: thin films, irradiation, photoluminescence, recombination, band-to-band.

1. Introduction

Cu(In, Ga)Se$_2$ (CIGS) is one of the most successful semiconductor compounds for the absorber layer of thin film solar cells. Laboratory size CIGS-based photovoltaic (PV) devices currently demonstrate record conversion efficiencies in excess of 23% placing this technology to a leading position for single junction thin film solar cells [1]. A *p*-type doping of CIGS is traditionally achieved by intrinsic defects introduced by deviations from the ideal stoichiometry [2]. High populations of such defects govern the electronic properties of CIGS and in turn the performances of CIGS-based solar cells. To improve further the performance of CIGS-based PV devices one should better understand the nature of intrinsic defects in this material. However, the nature of the majority of such defects has not been established experimentally as yet. It is mostly known from theoretical studies [3,4] whereas to become a guidance for technology developers theoretically obtained knowledge should be verified experimentally.

Irradiation of a semiconductor with high-energy electrons is a controllable method for an intentional introduction of intrinsic defects [5]. Lowing the temperature of such semiconductor during irradiation and its examination before and after warming to the room temperature can provide valuable information on primary defects (vacancies and interstitials) generated by irradiation, their recombination and the formation of more stable secondary defects [6].

The radiation hardness of CuInSe$_2$ and solar cells based on this material exceeds that of Si, GaAs and PV devices based on these semiconductors. Principal parameters of solar cells with CuInSe$_2$ absorber remained unchanged after irradiation of these cells with a dose of $2 \cdot 10^{16}$ cm^{-2} of 1 MeV electrons [7] whereas the conversion efficiency of solar cells with Si and GaAs absorbers after such a dose drops by about 40%. CIGS-based solar cells demonstrate a 25% conversion efficiency degradation after a dose of 1 MeV electrons as high as 10^{18} cm^{-2} [8]. The origin of such a stability of solar cells based on CuInSe$_2$ and CIGS against radiation is often attributed not to a hardness of the lattice of CuInSe$_2$ against radiation but to the ability of this material to heal the damage created by radiation [9,10]. However, physical mechanisms of such a healing has not been established as yet.

Photoluminescence (PL) is among the most efficient experimental techniques to study the nature of defects in semiconductors [11]. The effect of room temperature irradiation of CIGS thin films [12], CdS/CIGS heterostructures [13] and ZnO/CdS/CIGS/ Mo solar cells [14] by MeV electrons on PL spectra has been reported. However, no reports can be found in the literature on the influence of high-energy electron irradiation on PL spectra of CIGS films which are kept at cryogenic temperatures during irradiation.

In this report we study the effect of 10 MeV electrons on PL spectra of CIGS thin films kept during irradiation at 77 K, examined straight after irradiation by PL without

rising temperature and reexamined by PL again after warmed to room temperature.

2. Experimental Details

CIGS thin films were deposited on Mo coated soda-lime glass substrates by the co-evaporation of Cu, In, Ga and Se [15].

A scanning electron microscope (SEM) S-806 (Hitachi, Japan) was used to analyse the surface morphology of the films whereas an Oxford Instruments energy dispersive X-ray (EDX) microanalysis unit was employed to measure their elemental composition.

Measurements of the excitation intensity dependence of the PL spectra were carried out using a 60 cm base single grating (600 groves/mm) monochromator MDR-23. The 532 nm line of a 1 W KLM-532/h/1000 „Optronic" laser was used for excitation. A Peltier cooled Hamamatsu InGaAs $p-i-n$-photodiode, sensitive in the spectral range from 0.7 to 1.65 μm, was used to detect the PL emission. A lock-in amplifier along with a laser beam chopper were used to reduce the noise level.

PL measurements were carried out in 3 steps: (1) before irradiation PL spectra of the films were measuring at 77 K in a liquid nitrogen bath cryostat. After this the films were irradiated with a dose of $1.8 \cdot 10^{15}$ cm^{-2} of 10 MeV electrons at a current density of 10^{13} cm$^{-2} \cdot$s^{-1}. During irradiation the films were kept at 77 K in liquid nitrogen bath. (2) straight after irradiation PL spectra were remeasured at 77 K without raising the temperature. Then, during the 3rd step, the films were warmed up to the room temperature, cooled again to 77 K in liquid nitrogen bath and their PL spectra were measured again.

3. Results

Cross section and top view SEM images of the films are presented in Figs 1, a and 1, b, respectively. These images show a dense CIGS polycrystalline film with a thickness of 2 μm on a 1.2 μm thick Mo layer. The grain size was found to be in excess of 1 μm. The five-point average elemental composition (Cu 23.0, In 18.2, Ga 7.6 and Se 51.2 at%) suggests a copper deficiency of 0.89, determined from the ratio [Cu]/[In + Ga], a gallium content of 0.29, determined from the ratio [Ga]/[In + Ga], and a slight excess of selenium [Se]/[Cu + In + Ga] = 1.05.

Fig. 2 shows PL spectra, measured in similar optical conditions during the three stages of the PL measurements, on linear (a) and logarithmic scales (b, c). The spectra measured before irradiation reveal at 1.06 eV a broad dominant band with a full width at half maximum (FWHM) of 73 meV. The shape of this band suggests that it constitutes three merging higher intensity peaks P1, P2 and P3 at 1.12, 1.06 and 0.99 eV, respectively, as well as two lower intensity peaks: P4 at 0.88 eV and another peak with its maximum beyond the low energy sensitivity limit of the
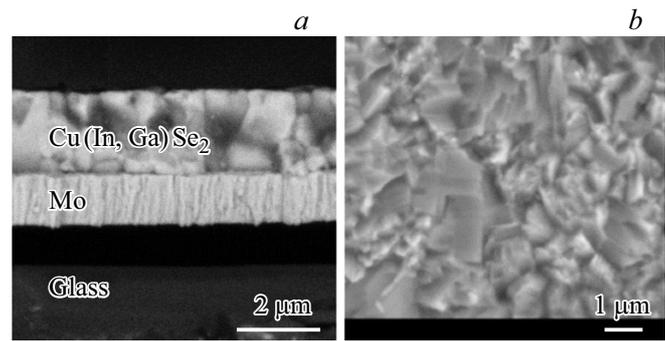
Figure 1. Cross section (a) and top view (b) SEM images of the CIGS film on Mo/glass substrate.

detector. Therefore, only the P1, P2, P3 and P4 peaks will be discussed below.

Fig. 2, a demonstrates that irradiation reduced the intensity of the dominant band by an order of magnitude whereas consequent warming of the films to the room temperature after irradiation doubles the intensity of this band. Fig. 2, b shows that irradiation did not induce in the PL spectra any new bands (within the studied spectral range). Fig. 2, c, where PL spectra, collected during the 3 steps of the PL measurements, are shown normalised by the maximum intensity of the dominant band, demonstrates that neither irradiation nor the subsequent warming shifted the dominant bands. However, Fig. 2, c shows that irradiation changes the shape of the dominant band suggesting that the intensity of the constituent P2 and P3 peaks is reduced by irradiation differently. Fig. 3 shows excitation intensity dependencies of the PL spectra. All the three sets of spectra reveal similar qualitative changes of the spectral shape with increasing excitation power: increasing intensity and clear blue shifts of the P2 and P3 peaks. On the other hand, the P4 peak does not shift.

To analyse mechanisms of radiative recombination of the P1, P2, P3 and P4 peaks as well as changes caused by irradiation the peaks were fitted by double sigmoid functions (DSF) proposed in [16]:

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

where A is an intensity scale parameter, whereas E_1, W_1, E_2 and W_2 are fitting parameters representing the shape of the low-energy (E_1 and W_1) and high-energy (E_2 and W_2) sides of each PL peak.

Fig. 3 demonstrates that P3 dominates the spectrum at low excitation levels whereas at the high levels P2 becomes the dominant peak. The use of double sigmoid functions makes it possible to estimate changes in the spectral position of the P2, P3 and P4 peaks with increasing excitation power for the three steps of PL measurements: before irradiation,
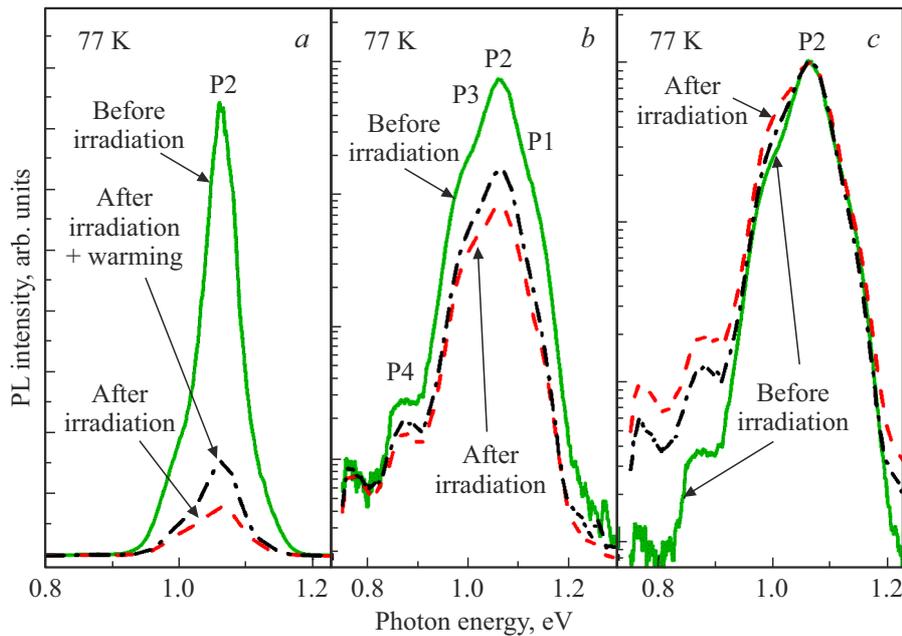
Figure 2. PL spectra of the CIGS films measured at 77 K before (step 1), straight after irradiation with a dose of $1.8 \cdot 10^{15}$ cm^{-2} without warming (step 2) and after irradiation and warming the films to the room temperature (step 3) on linear (*a*) and logarithmic (*b*) scales; normalised PL spectra (*c*) measured at power density of 20 W/cm^2.
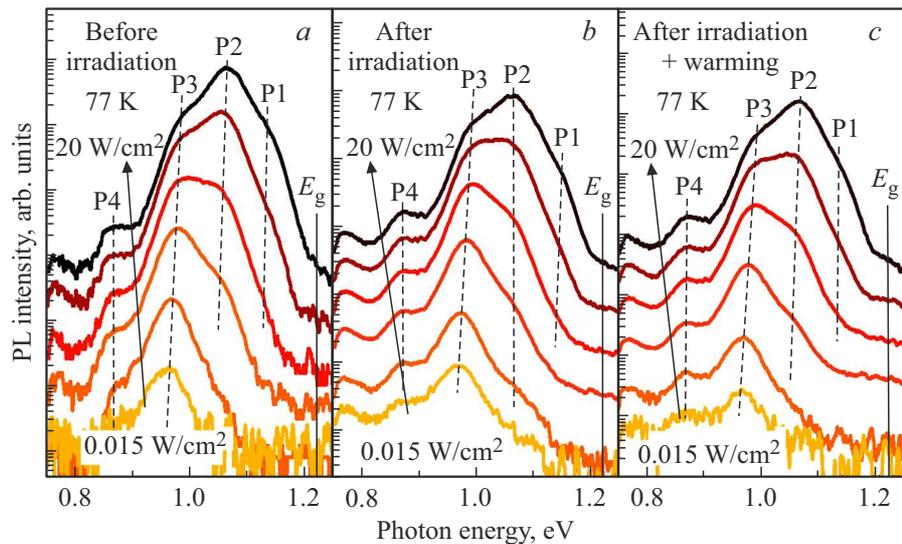

Figure 3. Excitation intensity dependences of PL spectra of CIGS thin films before (*a*) and after (*b*) electron irradiation in a liquid nitrogen as well as after warming the films to the room temperature (*c*).

straight after irradiation and after irradiation plus warming to the room temperature. The P2 and P3 peaks clearly blue shift with significant rates (j-shift per one decade of excitation power change). Before irradiation P3 demonstrates a blue shift $j(P3) = (12 \pm 2)$ meV/d. Neither irradiation nor the subsequent warming changed this value. A greater shift rate of $j(P2)_1 = (14 \pm 1)$ meV/d reveals before irradiation the P2 peak. Irradiation reduces sharply this value to $j(P2)_2 = (7 \pm 2)$ meV/d whereas the subsequent warming increases $j(P2)_3$ to (11 ± 1) meV/d. These values are also

shown in Table. Unlike the high intensity peaks P4 exhibits no shift at increasing excitation intensity.

The use of double sigmoid functions also makes it possible to estimate changes in the intensities of the PL bands more accurately. The intensity of a PL emission band $I(P)$ depends on the excitation laser power P as $I \sim P^k$, where k is a coefficient which can be determined from the gradient of $I(P)$ plotted on a log-log scale. The value of k can provide additional information about the nature of radiative recombination. Before irradiation

E_{max}, FWHM, *j*-shifts, *k* power coefficients of the P2 and P3 peaks before irradiation, after irradiation as well as after irradiation plus warming to room temperature

Peak		P2	P3
E_{max}, eV		1.063	0.993
FWHM, meV		62	56
W_1, meV		17	17
W_2, meV		14	14
j-shift, meV/d	1	14	12
	2	7	12
	3	11	12
k	1	2.2	1.2
	2	1.8	1.3
	3	2.1	1.6

the *k*-values of the P1, P2, P3 and P4 peaks were $k(P1)_1 = 2.6$, $k(P2)_1 = 2.2 \pm 0.1$, $k(P3)_1 = 1.2 \pm 0.1$ and $k(P4)_1 = 0.9 \pm 0.1$. Irradiation reduced *k* for the P1, P2 and P3 peaks to $k(P1)_2 = 1.5$, $k(P2)_2 = 1.8 \pm 0.1$, $k(P3)_2 = 1.3 \pm 0.1$ whereas *k* for P4 slightly increased to $k(P4)_2 = 1.0 \pm 0.1$. The warming increased *k* close to the values before irradiation $k(P1)_3 = 2.2$, $k(P2)_3 = 2.1 \pm 0.4$, $k(P3)_3 = 1.6 \pm 0.1$. For P4 the warming slightly increased *k* further to $k(P4)_2 = 1.1 \pm 0.1$. The reliable values of *k* for P2 and P3 are also shown in Table. P1 peak cannot be seen in the spectra at low excitation levels and even at high excitation levels it cannot be resolved suggesting a low accuracy of the determination of its parameters.

The bandgap (E_g) was estimated to be of 1.21 eV at [Ga]/[Ga + In] = 0.29 according to an empirical formula proposed in to describe the dependence of E_g on the content of Ga in CIGS films at 77 K [17].

4. Discussion

Copper deficient elemental composition of the CIGS absorber layer is important to achieve a high performance of CIGS-based solar cells [2,3] whereas a slight selenium excess is needed to avoid the formation of selenium vacancies, which have a detrimental effect on the minority charge carrier lifetime [4]. The about 30% of the gallium content provides an optimum bandgap for the absorber increasing with respect to CuInSe$_2$ but before the observed abrupt increase in the open circuit voltage deficit [18]. Thus, CIGS films with the elemental composition close to that in examined samples are of high technological importance.

The deficit of copper results in high probability of the formation of copper vacancies V$_{Cu}$, which are considered to be the main doping acceptors in CIGS [2–4], but also promotes the formation of the deep compensating donor, indium on copper site In$_{Cu}$, which can be neutralised by the

formation of the neutral defect complexes (In$_{Cu}$ + 2V$_{Cu}$) [3]. The presence of gallium leads to the formation of another deep compensating donor, gallium on copper site Ga$_{Cu}$, which is significantly deeper than In$_{Cu}$ and cannot be neutralised by V$_{Cu}$ [19]. High concentrations of charged defects can make semiconductors highly doped ones if the average distances between defects becomes smaller than their Bohr radii [20]. Charged defects generate spatial potential fluctuations leading to the formation of band tails. Although CIGS is a *p*-type semiconductor it also contains high concentrations of donors making this material a compensated semiconductor. The electron effective mass in CuInSe$_2$ $m_e^* = 0.09 m_0$ [21] (where m_0 is the free electron mass) is much smaller than that of the hole mass $m_h^* = 0.7 m_0$ [22]. Therefore, wave-functions of donor-like defects can already overlap at quite low concentrations making this material highly doped in terms of donors whereas the concentration of acceptors can still be much below the limit necessary for highly doped semiconductors in terms of acceptors [16]. The near band edge PL spectra of such a semiconductor can contain three emission bands: band-tail (BT) recombination of free electrons from the conduction band with holes localised at states in the valence band tail, free-to-bound (FB) recombination of free electrons from the conduction band with holes localised at acceptors with energy levels affected by potential fluctuations of the valence band and band-band recombination (BB) of free holes from the valence band with free electrons from the conduction band [23]. However, deep donors and acceptors, acting as charge carrier traps, can also be present. We are going to use this model to interpret the recombination mechanism of the peaks observed in our PL spectra.

The high *j*-shift values of the P2 and P3 peaks suggest that these peaks are associated with recombination mechanisms related to band-tails. We speculate that both peaks are related to the FB recombination whereas associated with two different acceptors. For the both peaks the *j*-shift exceeds significantly a 3 meV/d limit for donor-acceptor pair (DAP) recombination mechanisms [20]. Assigning P2 and P3 to band-tail related recombination mechanisms we can estimate from W_1 the mean depth of the valence band tail as $\gamma = 17$ meV. This value coincides with γ reported for single crystals of CuIn$_{0.5}$Ga$_{0.5}$Se$_2$ [16] but smaller than $\gamma = 30$ meV in Cu$_2$ZnSnSe$_4$ thin films [24]. Neither irradiation nor subsequent annealing induced noticeable changes of γ. It may mean that the defects generated by irradiation do not participate in the band tail. However, it also could be that the dose of electrons is not high enough to notice such changes.

According to our model the P1 peak can be preliminary assigned to the BB recombination. The value of *k* for P1, its spectral position as well as its shape can be taken only as estimates because this peak is not resolved in our PL spectra. According to [25] *k* values greater than unity can be attributed to a recombination type not involving defect localisations. Therefore, the high value of *k* for P1 suggests that this peak can be the band-to-band (BB) recombination.

BB bands are expected to be resolved in PL spectra measured at temperatures in excess of 130 K when other PL transitions reduce their intensity due to temperature quenching [16,20]. However, in PL spectra of $Cu_2ZnSnSe_4$ the BB transition was observed at temperatures below 10 K [26].

Irradiation of semiconductors by electrons with the energy high enough to generate displacement defects usually leads to a reduction of the carrier concentration and an increase in the level of compensation [27]. Therefore, the significant reduction in the intensity of the dominant PL band in our spectra can be due to deep, non-radiative defects which act as traps of charge carriers. A reduction of the charge carrier concentration has been observed in thin films of $CuInSe_2$ irradiated by 3 MeV electrons [28]. A reduction in the PL intensity, attributed to the formation of deep, non-radiative defects, was observed in PL spectra of thin films of $Cu_2ZnSnSe_4$ after irradiation by 10 MeV electrons [29].

The value of j in a semiconductor reflects the degree of compensation [11]. Copper deficient CIGS has a high degree of compensation. Although being a p-type material, it has both donors and acceptors [2]. Neither irradiation nor subsequent annealing changed the j value of P3. We attribute this to the nature of the acceptor associated with P3. We propose that irradiation did not influence such acceptors.

On the other hand, irradiation sharply decreases $j(P2)$ from 14 meV/d to 7 meV/d. This reduction can be due to a reduction of the compensation level caused by a radiation induced decrease in the concentration of donors or an increase in the concentration of acceptors associated with the P2 peak. This is an anomalous result. It suggests that the acceptor associated with P2 is influenced by radiation induced defects. We speculate that P2 is related to In_{Cu} which can be neutralised by two copper vacancies as predicted by [3]. After the room temperature annealing the degree of compensation increases and $j = 11$ meV/d reflects this increase.

The deep P4 peak does not change its spectral position with increasing excitation level. Therefore, it can be associated with FB recombination of free electrons with holes localised at deep defect levels. This deep level is not influenced by the valence band tails because of its depth. Therefore, it does not shift under increasing excitation level. We assign the P4 peak to recombination of free electrons with holes localised at a deep acceptor with an energy level 310 meV above the valence band possibly attributed to the double charged deep donor indium interstitial In_i^{++} [30]. This assignment is supported by the value of its k parameter. Irradiation and consequent warming did not change the spectral position of the deep P4 band. Also it did not affect the j-shift of this band.

The both high intensity peaks P2 and P3 demonstrate k values in excess of unity suggesting that their recombination mechanisms are not associated with defect-based localisation of the charge carriers such a DAP [25]. On the other hand, band-tail related emission bands often have their k values between two and unity [31] which supports our assignment for these peaks. The k values in excess of two for P1 and P2 can probably be explained by the achievement of a stimulated emission regime observed in CIGS thin films under high intensity pulse laser excitation [32]. To understand better this phenomenon temperature dependencies of the PL spectra should be measured and analysed.

The effect of room temperature irradiation of CIGS films by 5 MeV electrons with a dose of 10^{18} cm^{-2} was studied by PL at 4.2 K in [12]. Irradiation reduced the intensity of the dominant CIGS PL band and induced two new deep bands at 0.93 eV and 0.79 eV. PL spectra of CIGS-based solar cells measured at 77 K also revealed a new band at 0.93 eV after irradiation by 2 MeV electrons with a dose of 10^{17} cm^2 [33]. However, our PL spectra did not show any new peaks after irradiation. This can be because the dose of electrons was too low to induce in the PL spectra deep peaks with noticeable intensities similar to those which were observed earlier.

5. Conclusion

Thin films of $Cu(In, Ga)Se_2$ on Mo coated glass substrates, were irradiated by 10 MeV electrons with a dose of $2 \cdot 10^{15}$ cm^{-2} at 77 K. PL spectra before irradiation contained a broad dominant band at 1.06 eV, consisting of 3 peaks P1, P2 and P3. The P1 peak was assigned to the band-to-band recombination whereas the P2 and P3 peaks were preliminary assigned to the free-to-bound (FB) transitions.

Irradiation did not induce any new peaks in the PL spectra but reduced the PL intensity of the P1, P2 and P3 peaks, which is due to a reduction in the concentration of charge carriers captured at nonradiative defects, acting as deep traps, generated by irradiation. Irradiation did not change the j-shift of the P3 band suggesting that the acceptor, associated with P3, was not affected by irradiation. However, irradiation reduced the P2 j-shift from 14 meV/d to 7 meV/d demonstrating an anomalous effect of a significant reduction of the compensation level.

Warming to the room temperature doubled the intensity of the dominant band probably due to annealing of some radiation induced defects. It also increased the P2 j-shift to 11 meV/d, reflecting a rise in the compensation level after the annealing.

Ethics declarations

The authors declare that they have no conflict of interest.

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