Influence of electric field on photoluminescence of Cu(In,Ga)Se₂-based solar cells

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The photoluminescence (PL) of solar cells, based on Cu(In,Ga)Se₂ and bare Cu(In,Ga)Se₂ absorbers, has been studied. Shapes and intensity dependencies of the PL spectra in the junctions and in thin films are compared and discussed in terms of influence of the junction field. Measurements of the photoluminescence in the cells biased in the forward direction are employed in order to show straightforwardly how electric field changes the radiative recombination rate.

Keywords: solar cells, CIGS, photoluminescence.

1. Introduction

Most promising thin film solar cells technology is the one based on chalcopyrites from the Cu(In,Ga)(S,Se)₂ (CIGS) family. Record cells reach already 20% efficiency [1]. Among many methods of opto-electronic characterization employed for studying these cells and absorbers, photoluminescence (PL) measurements are often used. PL dependence on stoichiometry and composition of CIGS material has been extensively studied mainly in thin films or single crystals [2–9]. A dramatic difference has been found between the PL spectra of Cu-rich (with stoichiometry deviations Cu/(Ga + In) > 1) and Cu-poor (with deviations from stoichiometry Cu/(Ga + In) < 1) material. In CIGS layers, grown under Cu-rich conditions, the spectrum shows a number of narrow peaks identified as donor-acceptor, free-to-bound and excitonic transitions. The PL spectrum of the Cu poor material, commonly used in solar cells, exhibits very broad peaks, often merging into one featureless maximum. The intensity and temperature dependence of some of these PL maxima points towards an explanation being the fluctuating potentials in highly compensated, defected material [10–13].

PL in whole photovoltaic structures is of interest since it is a potential non-destructive tool for an in-line assessment of the absorber uniformity and quality [14]. Mapping the PL intensity shows non-uniformities in the microscale and problem regions in the device in which the non-radiative recombination is enhanced [15,16]. In order to better understand the origin of the PL non-uniformities, we should know more about changes of the PL efficiency and spectrum introduced by the junction field and presence of the hetero-interface.

In this contribution, we would like to examine the differences between the photoluminescence of complete baseline

cells in comparison to thin absorber films. We compare the PL results obtained in solar cells under open circuit conditions and under external dc bias to PL measured on the same absorbers after etching away the window layer.

2. Experimental details

Baseline photovoltaic structures of efficiency around 16%, fabricated at Angstrom Solar Centre (Uppsala University) were investigated. The structures consisted of a molybdenum back contact deposited on a soda-lime glass, Cu(In,Ga)Se₂ co-evaporated absorber layer (Ga/In = 0 and 0.3), CdS thin (50 nm) buffer layer deposited by chemical bath deposition, and sputtered i:ZnO followed by ZnO:Al window layer [17]. After characterization of a device, the window layer was etched away using 5% solution of HCl, and measurements were performed on the bare absorber.

For photoluminescence measurements we used a 488-nm line of Argon⁺ laser with excitation power in the range of 0.1 mW to 20 W. The photon density at the maximum laser power corresponds to the equivalent of 1 sun at AM1.5 (1 kW/m²s). A standard lock-in detection technique, employing a double grating monochromator MDR3 and an LNT-cooled germanium detector, was used.

Junction capacitance as a function of voltage bias was measured by the use of an HP 4284A LCR meter at ac frequency of 100 kHz.

We show here the results obtained at $T = 80$ K. This temperature was chosen as a compromise between the possibly good junction behaviour and in the same time PL emission efficiency high enough for detection in the above mentioned power range. Good junction behaviour is understood here as a lack of excessive distortion of capacitance-voltage and current-voltage characteristics due to high series resistance and/or carriers freeze-out occurring at very low temperatures.

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3. Results

PL spectra of the investigated cells and absorbers exhibit up to 4–5 poorly resolved peaks, with relative intensity changing with temperature and laser power. Their relative magnitude and shape exhibit some variation not only between samples but also from one point in the sample to another. This has been previously attributed to compositional inhomogeneities [15,16]. Basic features of the spectra are typical for the In-rich compositions of CIGS compounds. A representative example for 30% Ga baseline cell and thin film is shown in Figs. 1(a) and 1(b). The most prominent broad peaks in the 8–100 K range are those around 1.13 and 1.03 eV in ($E_g = 1.18$ eV as derived from spectral distribution of quantum efficiency measurements for this cell). Dependence of these peaks on temperature and light intensity, especially large blue shift with excitation power, is typical for radiative transition in the presence of fluctuating potentials [5–9]. After removal of the window layer by HCl etching, the shape of the spectra changes in comparison to one measured in the complete cell. Lower energy peaks are more pronounced in the etched sample and a band-to-band transition which has not been visible in the cell at 80 K appears in thin film at the highest light intensities. This behaviour has been observed in all samples studied, including pure CuInSe₂ cells, despite minor differences in the spectrum shape between the samples.

Fig. 1. Evolution of PL spectra with excitation intensity in 0.08–20 mW laser power range: (a) CIGS solar cell and (b) bare absorber.

In order to compare the PL dependence on excitation intensity we used a plot of spectrally integrated PL vs. laser power. We have not attempted here to resolve the intensity dependence for each peak separately because an error accompanying deconvolution in the case of broad, overlapping peaks is so large that it overcomes the advantages of more rigorous approach. Although one can observe that the highest energy peak in thin film corresponding most probably to band-to-band transition increases faster than others at highest laser powers, the effect is negligible at lower laser powers and so does not influence significantly the results. In Fig. 2, an example obtained for CuInSe₂ cell and bare absorber is shown. The dependence is superlinear in the intermediate region between low and high intensities comparing to 1 sun in contrast to (almost) linear increase for thin films after removal of window layer. We attribute this to the influence of the junction field on the radiative recombination rate. In order to demonstrate this, we measured spectrally integrated PL in the junctions as a function of the external dc voltage bias. We used low laser power (typically 0.8 mW) to ensure that little change was introduced by illumination itself to the electric field distribution in the junction. A significant increase in more than an order of magnitude was observed in the PL signal at forward biases approaching flat band conditions comparing to the reverse or 0 V bias (at short circuit conduction). As shown in Fig. 3, this increase takes place when the depletion layer width calculated from the junction high frequency capacitance decreases below 250 nm. Since the depleted n-type part of the junction consisting of undoped CdS and i-ZnO layers is about 100 nm, it follows that depleted region in the absorber drops then below 150 nm. These results are qualitatively similar as obtained by EMPL method for CuGaSe₂ epitaxial and polycrystalline absorbers [18] although here we show PL intensity measured in the biased junctions under steady-state conditions, without using any voltage modulation.

Fig. 2. Spectrally integrated PL intensity as a function of laser power in CuInSe₂-based solar cell (open symbols) and in the bare absorber (closed symbols) at 80 K. Broken lines are linear fits to the experimental data, solid line in case of the cell serves as a guide to the eye.

Fig. 3. Spectrally integrated PL intensity (triangles) and depletion width (circles) of a cell as a function of external dc voltage bias.

Since the electric field in the junctions is reduced under illumination, the dependence of the PL intensity on the excitation power is more complicated in the devices than in thin films. The hypothesis that charge separation in the junction electric field is the main reason for the non-linear PL power dependence in the devices for excitation intensities below 1 sun has been verified by measurements of PL power dependence in the devices under flat band conditions. In Fig. 3, three dependencies of the spectrally integrated PL) measured for baseline Cu(InGa)Se₂ device and bare absorber (Ga content around 30%) as a function of laser power are shown. The data for the unbiased device (open circuit conditions) and for the device biased in the forward direction up to the flat bands conditions are compared to the results obtained for the same sample after etching. Super-linear behaviour is observed in the open-circuited device. In both

Fig. 4. Dependence of spectrally integrated PL intensity on excitation power measured in baseline CIGS device: open-circuited unbiased device – triangles, forward biased device – open circles, bare absorber – close circles. Broken lines are linear fits, line connecting experimental points for open-circuited devices is shown as a guide to the eye.

thin film and in the forward biased device under flat band conditions, a linear dependence is observed for all photon fluxes. We conclude that non-linear dependence in the device under open circuit conditions is caused by the gradual decrease in the effective junction field caused by the laser beam of increasing intensity.

4. Discussion

We observe a significant influence of the junction field on PL intensity. This influence has been also observed by Metzger [19]. In Ref. 19, it was noticed also that PL is more efficient in the devices than in thin films exposed to air. This observation agrees also with our results, even though in our experiments the sequence of measurements was different: we measured first the whole devices and then bare absorbers after etching and in Ref. 19, first the bare absorbers were measured and then deposition of the window layer took place. Our results show the possibility that spatial variation of the PL intensity at low excitation power in the cells and minimodules could originate not only from spatially varying contributions of non-radiative recombination but also from spatial variations of the junction electric field.

An interesting feature is a difference between the PL spectra observed in the complete cells and in corresponding bare absorbers, lower energy peaks dominate in thin films comparing to the cells. Two mechanisms might be held responsible here, a different Fermi level splitting in the presence of Fermi-level pinned close to conduction band at the heterointerface or a different defect spectrum in the device compared to thin CIGS film. The latter mechanism might be explained by theoretical work by Lany and Zunger [20] which predicts that distribution of energy levels belonging to selenium vacancies or $V_{Se}-V_{Cu}$ defects due to their negative-U property depends on the position of the Fermi level with respect to the energy of defect conversion from shallow donor to shallow acceptor configurational state. Hence in a device in the depletion region, more V_{Se} in the shallow acceptor state than in p-type thin film is expected. If one from the observed transitions involves this acceptor level, then its intensity should be reduced in thin film comparing to solar cell. The influence of position and pinning of the Fermi level at the heterointerface in the solar cell on Fermi-level splitting in the device should also be taken into account.

5. Conclusions

We show here the differences between photoluminescence spectrum, intensity, and dependence on the excitation power between solar cells based on CIGS and bare absorbers after etching away the window layer. The latter effect we attribute to the influence of the electric field on the radiative recombination rate and conclude that variation of the junction field should also been taken into account when discussing PL spatial non-uniformities at low laser power. The comparison between spatially-resolved photoluminescence

at low and high laser power (comparing to 1 sun equivalent) might provide additional information on the sources of photovoltaic losses in the microscale. We also indicate the possible sources of the differences between spectral distributions, namely differences in the concentration of the V_{Se}-related levels associated with donor and acceptor configurational state in thin films and devices and/or different Fermi-level splitting in the presence of the heterointerface. Exploration of this issue is now a subject of further work.

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