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Photoluminescence study of ZnO/CdS/Cu(In,Ga)Se_2 solar cells

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Photoluminescence (PL) of the absorber layer of ZnO/CdS/Cu(In,Ga)Se_2 solar cells has been studied. Baseline process solar cells as well as structures subject to a damp heat treatment and sodium-free structures have been investigated. The excitation intensity and temperature dependence of the photoluminescence spectra have been measured. A large blue shift of the photoluminescence bands for increasing excitation intensity has been observed with a per decade shift value ranging from 10 meV for baseline cells to 35 meV for Na free cells. This is characteristic behaviour for spectral bands due to transitions involving random potential fluctuations in highly compensated In-rich near-interface layer of the Cu(In,Ga)Se_2 film. The temperature evolution of the spectra indicates two types of PL transitions: the tail-impurity and band-impurity transitions. The change of the PL spectra upon the damp heat treatment is discussed.

Keywords: thin film solar cells, photoluminescence, defect states.

1. Introduction

Structural defects have a profound effect on performance of ZnO/CdS/Cu(In,Ga)Se_2 solar cells [1]. Photoluminescence measurements offer an opportunity to study defect states in the absorber layer of the ready-made ZnO/CdS/Cu(In,Ga)Se_2 solar cells. In fact, considering the penetration depth of the exciting light, we test only a fraction of micrometer thick active interface layer close to CdS buffer. PL gives an account of radiative recombination processes via relatively shallow defect states. Apart from spectral properties of the PL, the total emission efficiency is also important parameter for the cells, indicating relative contribution of radiative and non-radiative recombination. PL has been thoroughly studied in thin films of Cu(In,Ga)Se_2 (CIGS) [2–6]. Photoluminescent properties of such films depend strongly on their stoichiometry. In-rich CIGS films exhibit PL typical for heavily compensated semiconductors.

Relatively few papers have been devoted to PL studies of the CIGS based solar cells. Long-term stability of solar cells is examined under severe lifetime testing conditions known as damp heat test. PL technique is used for studying alteration of the absorber layer due to degradation processes.

In this paper we studied photoluminescence of the absorber layer of baseline ZnO/CdS/Cu(In,Ga)Se_2 solar cells as well the cells with Na-free absorber and the cells subject to damp heat treatment.

2. Experimental

The investigated cells have been prepared at Angstroem Solar Centre of Uppsalla University. The Cu(In,Ga)Se_2 absorber layer has been deposited by the co-evaporation [7]. The baseline process yields cells with efficiency between 14% and 15%. Baseline cells have been prepared on soda lime glass. Na-free absorber layers were prepared after depositing sodium diffusion barrier of Al_2O_3 on soda lime glass. Some of baseline cells were subject to damp heat treatment (1000 h, temperature 85°C, 85% humidity) described in detail in [8]. Upon the treatment the efficiency of the cells decreased from 14% to 7%. The PL has been excited by a 514 nm line of Ar^+ laser. The germanium liquid nitrogen cooled detector has been used. Measurements have been carried out using closed-cycle refrigerator in the temperature range 8–300 K. The excitation power dependence and temperature evolution of the PL spectra have been studied.

3. Results and discussion

3.1. Baseline cells

PL spectra of baseline cell with the efficiency of 15% for varying excitation power are shown in Fig. 1. The spectra for almost all excitation powers consist of the broad band B with a weaker spectral structure seen at the low energy part A. At lowest laser excitation intensities both bands are comparable in the intensity with a third band visible at high energy side of the spectrum C. We deconvoluted the spectra into separate bands assuming the Gaussian spectral pro-

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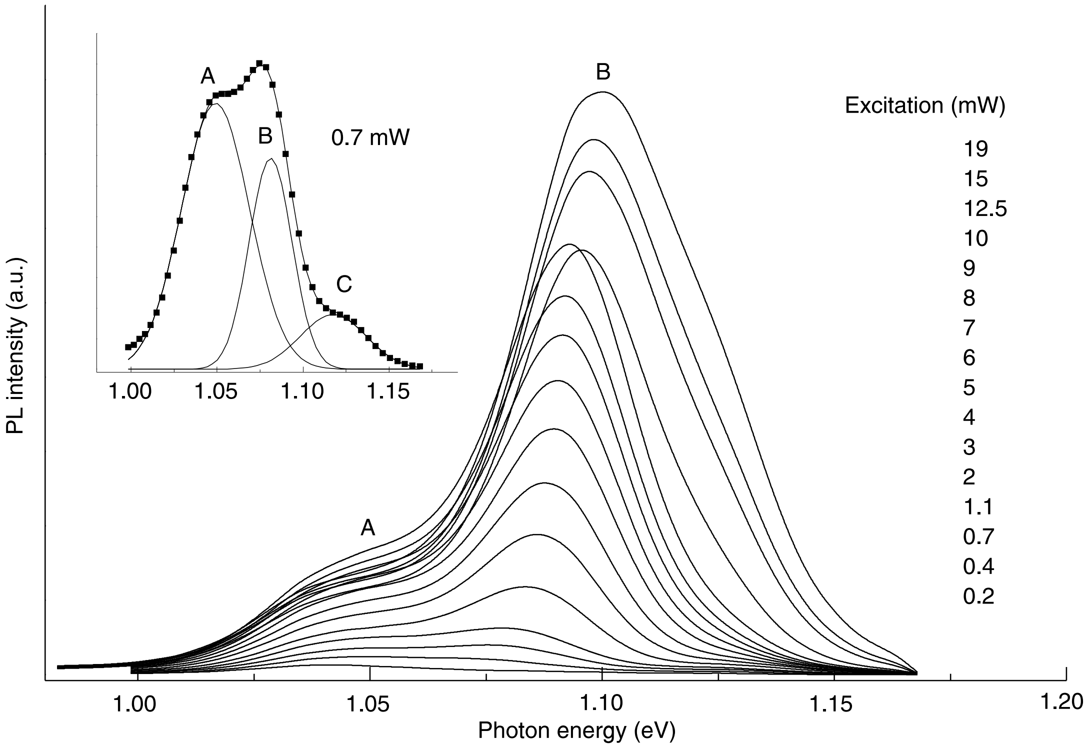

Fig. 1. PL spectra of a baseline cell for varying excitation power. Inset shows the spectrum for the excitation power of 0.7 mW.

files. However, such a procedure did not produce univocal results for all excitation intensities. Especially, it was difficult to separate a contribution of the C band. The bands exhibit a blue shift for increasing excitation intensity (Fig. 1). The excitation intensity I_{exc} dependence of the B band energy E_{max} is presented in Fig. 2. Usually, such dependence is described by the approximate expression

$$I_{exc} = I_0 \times 10^{E_{\max}/\beta}$$

As it can be seen from Fig. 2, the experimental E_{max} – $log(I_{exc})$ plot is nonlinear for higher excitation intensities. The straight-line approximation of the lower intensity part gives the factor (PL shift per decade of laser power) about 10 meV with much higher slope at higher intensity part. Similar behaviour exhibits the weaker band A. Such a large blue shift is characteristic for PL of highly defective and compensated semiconductors. The radiative transitions in such materials involve potential fluctuations due to charged defects superimposing the valence and conduction bands (and followed by shallow defect levels). The energy shift constant β is proportional to the depth of the potential fluctuations. These transitions have been observed in heavily compensated semiconductors (e.g,. GaAs in Ref. 9) and are referred to as quasi-donor acceptor (QDA) transitions as opposed to typical donor-acceptor pair (DAP) recombination [9]. The latter is characterized by a much lower value of the β factor (less than 5 meV).

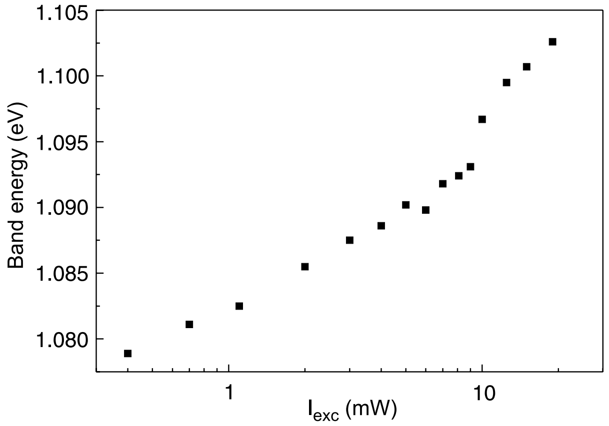

Fig. 2. Excitation power dependence of the main band energy (B) for a baseline cell.

The luminescence related to the potential fluctuations differs from DAP recombination also in its temperature dependence. Figure 3 shows temperature dependence of the PL peak energy. The A band exhibits the red shift and B band exhibits the blue shift with increasing temperature. Both types of temperature dependence of the PL band position have been observed in In-rich CIGS films depending on temperature range and excitation power by Dirnstorfer *et al.* [3]. The PL emission is explained in terms of two types of transitions: at low temperatures and moderate excitation power the tail-impurity (TI) recombination between electrons localized at donor clusters and holes at acceptors dominates. At higher temperatures and/or higher excitation power the recombination involves electrons in conduction band and acceptor levels (band-impurity BI recombination). Temperature dependence of transition energy is different for both types of recombination – for TI

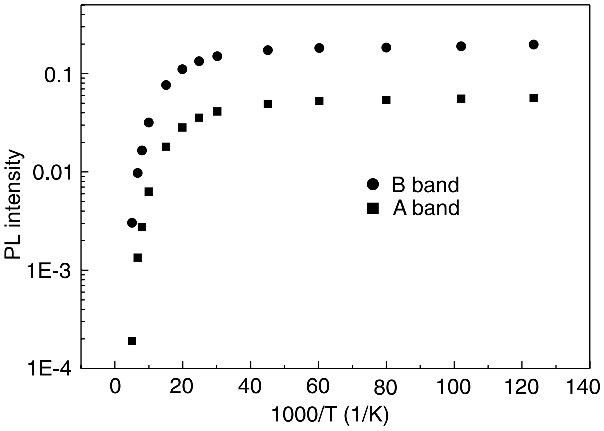

Fig. 3. Temperature quenching of the PL for the excitation intensity of 10 mW.

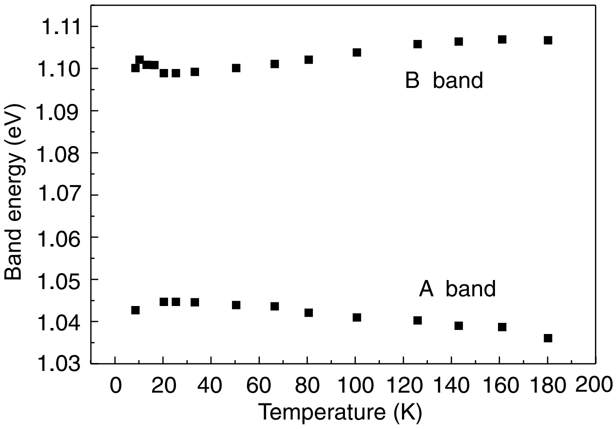

Fig. 4. Band energies vs. temperature for a baseline cell.

recombination a red shift is expected and a blue one for the BI recombination.

The proposed model can explain excitation power and temperature dependence of the PL band observed in our study. However, differently than in Ref. 3, where a single band has been observed, at least two bands are discernible in our spectra. The B peak bears all attributes of band-impurity recombination (blue shift with increasing temperature). The A peak shifts to lower energies at higher temperatures as can be expected for tail-impurity recombination. This can be interpreted as due to two different donor states – a very shallow one merging with the conduction band and a second one about 50 meV below the conduction band. The probable candidates for the shallow donor are selenium vacancies V_{Se}. Deeper donor states can be due to (In_{Cu} + V_{Cu}) pair or to second ionisation level of V_{Se} [10].

The thermal quenching of the PL is observed for temperatures above 50 K. The plot is very similar for both emission bands (Fig. 3). The Arrhenius plot is linear only for a few points at highest measurable temperatures with an activation energy of 22 meV for 3 mW excitation power and 26 meV for 10 mW excitation. The thermal quenching of PL is usually related to a thermal release of carriers trapped at localized recombination centres. It seems that ionisation of the contributing acceptor state is responsible for the quenching in the temperature range used, so the obtained values give a rough estimate of the acceptor ionisation energy.

3.2. Na – free cells

The remarkable feature of the PL of sodium free cells is the emission intensity roughly 50 times smaller than for the absorber layers grown on sodium glass. Normalized PL spectra of both types of cells are compared in Fig. 4. The PL band of Na-free cell is much wider (it extends to lower photon energies) than that of standard cell. The blue shift of the PL band with increasing excitation intensity is also much higher (β factor is 35 meV). The thermal quenching starts at much lower temperatures and its activation energy is lower (*ca.* 4 meV) than for the cells with the Na doped absorber.

Sodium is known to induce various changes in CIGS absorber layers: it improves film morphology, reduces compensation and increases the effective hole density [11]. Our observations indicate that lack of Na in absorber layer leads to increased potential fluctuations and to creation of non-radiative recombination centres. The much lower thermal quenching activation energy than for the baseline cells indicates, that sodium removes shallow donor states. It also agrees with theoretical predictions of Su-Huai Wei *et al.* [11] who stressed that the main role of Na is the passivation of compensating donors.

Our results are in variance with PL results of Dirnstorfer *et al.* [5], who found no changes in PL for Na doped and Na-free films.

3.3. Damp heat treated cells

After damp heat treatment of the standard cell its PL intensity drops ~25 times. Apart from the small spectral shift towards higher energy the general structure of the spectra is similar as for low excitation intensity spectra of baseline cells (Fig. 5.). Opposite to the results of the PL study of Medvedkin *et al.* [12], the high energy peak at 1.17 eV is more pronounced for the damp heated samples than for the baseline cells. Deterioration of the window (ZnO) and buffer (CdS) layers found for damp heated cells in Ref. 12 cannot explain such a strong decrease in the PL signal. The junction capacitance techniques and electron transport measurements [13,14] indicate that the damp heating introduces deep electron traps in the absorber layer. They act as non-radiative recombination centres killing the PL emission intensity. Differently from the PL spectra of the baseline cells, the position of three PL bands in damp heated cells hardly depends on the excitation power (Fig. 6). Only for the highest energy peak a slight increase of the energy position with increasing excitation is observed. Such a behaviour resembles the PL of In-rich films of Cu(In,Ga)Se_2 annealed in air [6] when the “flatband condition” is achieved. It has been suggested that the air annealing re-

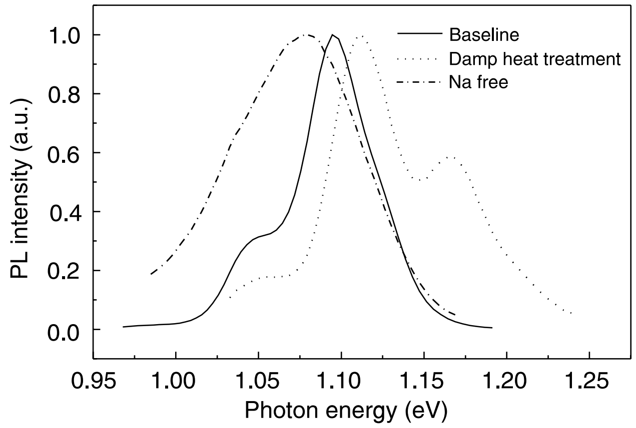

Fig. 5. Comparison of the normalized spectra for the baseline, Na-free, and damp-heat treated cells.

duces degree of compensation by lowering the donor concentration. A probable process for donor passivation includes formation of O_{Se} defects [6]. The latter are electrically inactive deep acceptor centres. This leads to a change from the recombination between fluctuating potentials for an as-grown film to donor-acceptor pair or free-to-bound transitions. It seems that the damp heat treatment has a similar effect on baseline cells, apart from producing deep centres of nonradiative recombination. It is a subject of the ongoing study.

4. Conclusions

The photoluminescence spectra of the absorber layer of the baseline $ZnO/CdS/Cu(In,Ga)Se_2$ solar cells are characteristic for highly compensated semiconductor film with potential fluctuations of the order of 10 meV. Comparison with devices prepared on the Na-free glass indicate that the lack of Na in the absorber layer increases degree of compensation and lowers film quality. Damp heat treatment introduces non-radiative recombination centres, reducing light emission intensity. Spectral changes are similar as for air annealed In-rich $Cu(In,Ga)Se_2$ films.

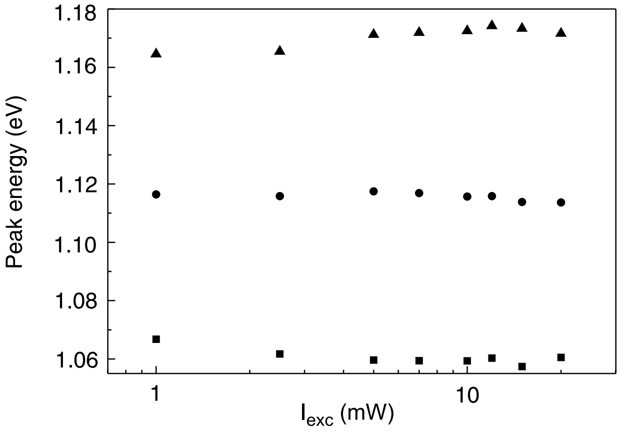

Fig. 6. Excitation power dependence of the band energies for the damp heated cell.

Acknowledgments

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