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The Influence of Metastabilities on the Luminescence in the $Cu(In,Ga)Se_2$ Solar Cells

D. Prządo[a,*], M. Igalson[a], R. Bacewicz[a] and M. Edoff[b]

[a]Faculty of Physics, Warsaw University of Technology
Koszykowa 75, 00-662 Warsaw, Poland
[b]Uppsala University, Ångström Solar Center, Sweden

Photoluminescence and electroluminescence spectra of the absorber layer in $ZnO/CdS/Cu(In,Ga)Se_2$ solar cells were measured. Their dependence on temperature, excitation intensity and applied voltage were studied. Electroluminescence measurements were used to investigate light- and bias-induced metastabilities in the absorber of the cells. We showed that metastable changes of defect distributions, which produce an effect on the electrical characteristics of $ZnO/CdS/Cu(In,Ga)Se_2$ material, affect also the luminescence yield. The dependence of the intensity and shape of the electroluminescence spectra on the state of the sample is observed. These results fit well into the theoretical calculations of Lany and Zunger model showing that divacancy complex (V_{Se}–V_{Cu}) is responsible for metastable changes observed in $ZnO/CdS/Cu(In,Ga)Se_2$-based solar cells. We conclude that during light soaking or/and forward bias the probability of nonradiative recombination is decreased.

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1. Introduction

Thin film technology of photovoltaic devices is material- and cost-efficient alternative to standard, silicon-based solar cells. To the most promising novel solutions belong thin film solar cells based on chalcopyrite compounds belonging to $Cu(In,Ga)(S,Se)_2$ (CIGS) family. They approach 20% photovoltaic conversion efficiency and are presently entering a commercialization phase on wider scale. Despite this success, defect physics of CIGS absorbers is still far from being well understood. One of the puzzling phenomena are metastable effects observed after illumination and/or voltage bias applied at room temperature in many electrical characteristics of the cells, namely in current–voltage characteristics, admittance

*corresponding author; e-mail: daniello@if.pw.edu.pl

and deep level transient spectra (DLTS), capacitance–voltage profiles, etc. [1–7]. These effects are persistent below 200 K and indicate that a redistribution of defect levels takes place under illumination or voltage bias. The mechanism of metastable effects has been under dispute for more than 10 years already. Recently they have been attributed to the negative-U behavior and large lattice relaxation of a divacancy defect $V_{Cu}-V_{Se}$. Theoretical calculations from the first principles by Lany and Zunger (L–Z) [8, 9] have shown that the unoccupied positively charged defect introduces shallow donor level, while negatively charged one, after undergoing pronounced configurational change, becomes shallow acceptor. Additionally, the defect in the acceptor configuration introduces into the gap another level associated with the antibonding state, situated about 0.88 eV above the valence band.

One straightforward consequence of L–Z model is a non-uniform distribution of charged defects in the thermal equilibrium conditions within the absorber layer (Fig. 1a) [10]. One might expect that close to the interface, the acceptor configuration prevails, while further away from the interface, almost all defects are in the donor state. Very close to the interface even antibonding levels are occupied producing a thin layer of the negative charge. A prolonged illumination of the device produces metastable changes in this distribution, namely the concentrations of defects in the acceptor and donor configuration becomes more uniform through the active region of the absorber (Fig. 1b). Hence various electrical characteristics of the junction, in particular also its transport properties and photovoltaic parameters, are affected.

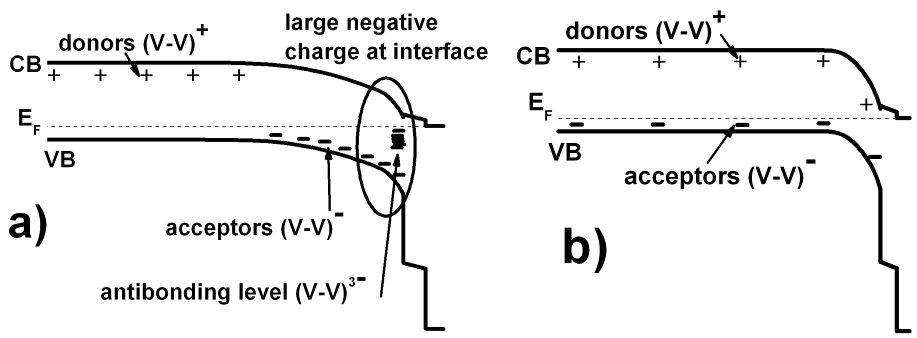

Fig. 1. Band diagram of charged defect distribution according to the Lany–Zunger model: (a) relaxed state, (b) light soaked state.

The important question arises now whether the distribution of defects in the two configurational states affects the recombination of non-equilibrium carriers in the device. Investigation of luminescence properties of the device might be a tool here, but illumination necessary for investigation of photoluminescence (PL) is most effective also in producing the metastable state. Therefore, we have chosen electroluminescence (EL) as a tool for investigation of the influence of metastable distributions of defect levels on the radiative recombination probability.

2. Experimental details

The samples were baseline $ZnO/CdS/Cu(In,Ga)Se_2$ structures prepared according to the standard recipe in the Ångström Solar Center, Uppsala University, with the CIGS absorber layer obtained by co-evaporation from the elemental sources on molybdenum-covered glass substrate. CdS buffer layer was obtained by chemical bath deposition and followed by sputtered ZnO window. Al–Ni grid completed the structure [11].

The sample was mounted inside a closed cycle He cryostat. For PL measurements we used the 488 nm line of Ar^+ laser with the excitation power in the range between 1 mW and 200 mW. EL measurements have been performed in the ac bias voltage range up to 1.7 V corresponding to the current injection levels of up 0.2 A/cm^2. The EL and PL spectra have been measured with the use of a computer controlled MDR3 grating monochromator with the focal length of 0.6 m and a liquid nitrogen temperature cooled (LNT-cooled) germanium detector. A conventional lock-in detection has been employed.

Light soaking has been performed by using illumination provided by a halogen lamp with intensity similar to working conditions of the cell (1 kW/m^2).

3. Results

Both PL and EL spectra as a function of excitation intensity and temperature have been investigated. Both methods detected the same channels of radiative recombination as shown in Fig. 2. The normalized PL (upper curve) and EL (lower curve) measured at 100 K for the same standard CIGS sample with 30% Ga content are here depicted. Two main emission channels are detected at 1.03 eV (QDA1) and 1.1 eV (QDA2). The broad QDA1 and QDA2 transitions are due to a quasi-donor-acceptor recombination, which is confirmed by a typical in that case large shift of the peak energies to higher values with increasing excitation power. This feature is illustrated in Fig. 3 and agrees well with other reported data [12, 13]. We assumed Gaussian function to describe spectral shape of the observed PL bands. It is an approximation since most of the PL bands have an asymmetrical shape [14]. Shallow acceptor levels involved in these transitions are probably V_{Cu} and V_{Se} [13]. At higher temperatures the third peak at 1.17 eV (BB), corresponding to band-to-band recombination, appears (see Fig. 2).

In order to investigate the influence of the metastable state of the device on the luminescence yield, we have measured the EL spectra after so-called "light soaking" (1 h illumination at 300 K followed by cooling to 80 K under illumination) and then after a sequence of annealing treatments. The results are presented in Figs. 4 and 5. In Fig. 4 the total area of the EL intensity is plotted against the injection current I_{inj} after light soaking, after subsequent heating the sample to 270 K and cooling down again, and after another heating to room temperature followed by cooling down to the measurement temperature of 80 K. The slope of these dependences decreases after gradual annealing at 270 K and 330 K. Since

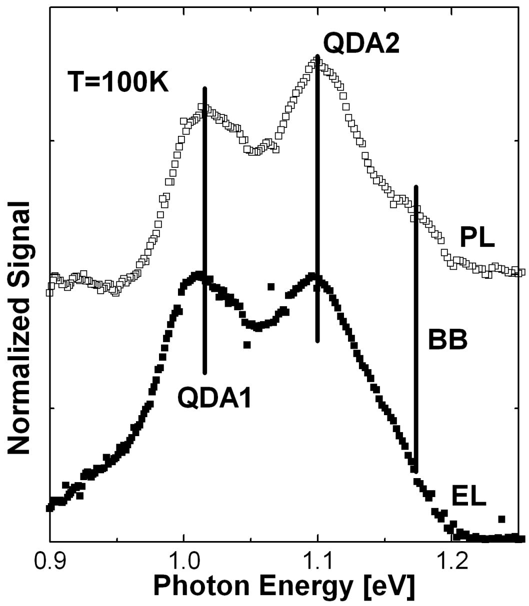

Fig. 2. Comparison of the normalized photo- (□) and electroluminescence (■) spectrum for the CIGS sample at 100 K. The measured spectra show 3 bands close to 1.0 eV (QDA1), 1.1 eV (QDA2) and about 1.17 eV (BB).

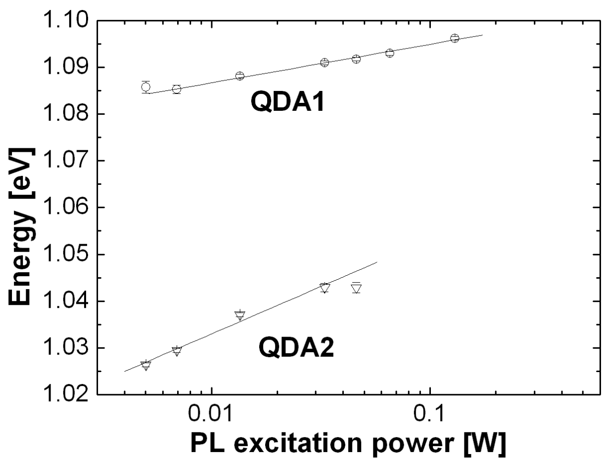

Fig. 3. Peak position evaluation as a function of the laser excitation for the CIGS sample at 8 K.

the EL intensity depends on the ratio of probabilities of radiative to nonradiative transition

$$I_{\mathrm{PL}} \propto I \frac{P_{\mathrm{rad}}}{P_{\mathrm{nonrad}} + P_{\mathrm{rad}}},$$

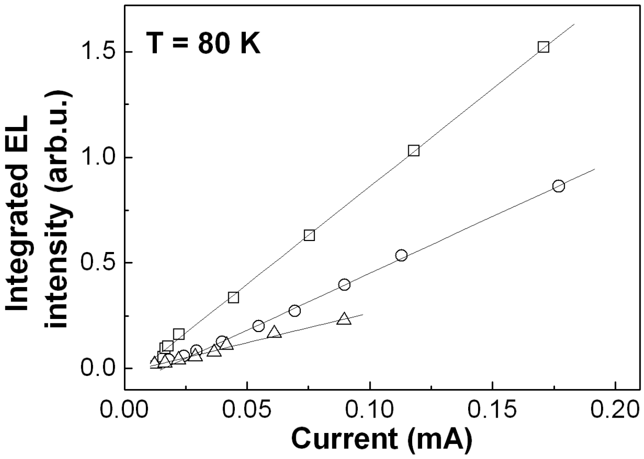

Fig. 4. Integrated electroluminescence signal as a function of the injection current for CIGS sample at 80 K for three different metastable states: (□) light soaking, (○) after short annealing at 270 K, (△) after short annealing at 270 K and 300 K.

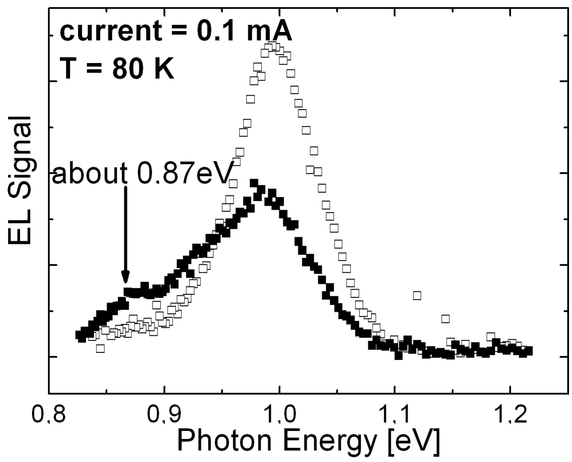

Fig. 5. Electroluminescence spectrum of CIGS sample at 80 K with injection current 0.1 mA for two metastable states: (□) light soaking, (■) after short annealing at 270 K.

we conclude that annealing causes an increase in the probability of nonradiative recombination. It has to be emphasized that in the relaxed state of the device, reached after annealing the sample at 330 K, the EL intensity dropped below the detection limit.

In Fig. 5 the EL spectra measured at the same injection current of 0.1 mA at 80 K measured for two states of the sample are shown, after light soaking and after annealing at 270 K. We notice that when the thermal equilibrium is approached, not only the probability of nonradiative recombination increases, but also a low-energy peak becomes noticeable in the spectrum. The energy of that peak, 0.87 eV, agrees well with the transition energy between the antibonding level of V_{Se}–V_{Cu} in the acceptor configuration.

4. Conclusions

We have observed for the first time that there is a relation between the state of the CIGS photovoltaic device and the magnitude and the shape of the electroluminescence spectrum. Annealing of the sample in steps from the light soaked state to the (almost) relaxed state increases significantly the recombination via nonradiative centers. This might be explained as due to the increase in the interface recombination in the relaxed state of the device resulting from non-uniform distribution of the electric field due to thermal equilibrium distribution of metastable defects (Fig. 1a). The alternative explanation is that the concentration of nonradiative recombination centers (V_{Se}–V_{Cu}) defects in the acceptor configuration increases after annealing. While we cannot distinguish between those two effects in our experiment, both should lead to the decrease in photovoltaic efficiency of the CIGS devices, and thus they agree well with the observation that light soaking improves performance of these cells [2, 6, 15].

Furthermore, in the relaxed state of the device we have observed the low-energy emission, which might be attributed to the antibonding level of double vacancy in the acceptor configuration. According to Lany and Zunger [8, 9], this configuration should prevail in the interface region of the device in thermal equilibrium, while light soaking should decrease the amount of this state.

Summing up, our experiments show some of the consequences of a presence of the metastable defects on the most important property of the solar cell — the dominating recombination mechanism in the device.

Acknowledgments

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