Thin Solid Films xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Simulation of metastable changes in time resolved photoluminescence of Cu(In,Ga)Se_2 thin film solar cells upon light soaking treatment

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ARTICLE INFO

Article history:
Received 9 May 2016
Received in revised form 17 August 2016
Accepted 18 August 2016
Available online xxxx

Keywords:
Transient photoluminescence
Simulation
Solar cell
Cu(In,Ga)Se_2
Metastability

ABSTRACT

Cu(In,Ga)Se_2 thin film solar cells are known to show a metastable behavior of their open circuit voltage when exposed to light. Time resolved measurements of the photoluminescence decay after pulsed excitation (TRPL) reveal that also the photoluminescence decay (PL) changes with conditioning, yielding shorter effective lifetimes after annealing under illumination (light soaking) than after annealing in the dark. By using time resolved device simulations we applied a model that explains the TRPL metastable behavior. For this we used a model of capture and reemission of minority charge carriers via two characteristic trap states near the conduction band, while also accounting for changes in trap density and doping concentration caused by light soaking. To further understand the mechanisms behind PL decay we analyse the influence that the charge carrier dynamics play in TRPL decay by a variation of select simulation parameters.

1. Introduction

Annealing of Cu(In,Ga)Se_2 (CIGSe) thin film solar cells under illumination (light soaking) can have an effect on their efficiency and open circuit voltage [1]. Time resolved photoluminescence (TRPL) measurements offer a possibility to investigate the recombination mechanisms and charge carrier dynamics in this material [2], while simulations can yield more information about the influence of these processes on the measured TRPL decay [2–6]. We try to achieve a better understanding of metastability in CIGSe solar cells using a simulation by analysing the changes in charge carrier dynamics after light soaking and how these affect TRPL behavior.

In this work we consider the results of TRPL measurements of CIGSe thin film absorber layers passivated with a CdS buffer layer and compare them to simulations carried out for the same layer configuration. We try to simulate the intensity dependent TRPL behavior by accounting for changes in doping concentration, concentration of trap states near the conduction band and activation energy of those states, as observed by capacitance-voltage characterization and admittance spectroscopy. Finally, we analyse the impact of the absorber doping concentration as well as recombination and capture parameters on TRPL decay in our simulation model to draw some conclusions about the influence of charge carrier dynamics on photoluminescence decay.

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2. Experimental details

2.1. Characterization

Measurements were performed on solar cells from industrial preparation. The samples consist of a glass substrate with a 0.4 μm thick molybdenum layer as a back contact, a coevaporated CIGSe absorber layer with a thickness of 1.92 μm, a 65 nm thick CdS buffer layer, and window layers of 70 nm thick i-ZnO and 0.87 μm aluminum-doped ZnO. More information about the preparation can be found in Ref. [7]. For the CIGSe layer, a linear [Ga]/([Ga]+[In]) gradient was determined via glow-discharge optical emission spectroscopy measurements. The effect of this gradient on the band gap of the CIGSe layer can be seen in Table 1.

All samples were annealed in the dark for 15 h at a temperature $T = 90$ °C. This state is labeled as "dark-annealed" (DA). Some of the samples were further annealed under illumination or "light soaked" (LS) for 9 h using an AM1.5 solar simulator.

The long treatment times were chosen to guarantee the reversibility of the process, since the doping concentration of the CIGSe absorber reaches levels close to saturation after such treatment. Additional samples were annealed in the dark again after having been light soaked in order to investigate the reversibility of the process. While the doping concentration is increased by a factor of 12 after light soaking (see Table 1), the doping concentration of the samples dark-annealed for a second time after light soaking is changed by a much smaller factor of 1.23 when compared to the samples dark-annealed once. Therefore we consider the process to be fairly reversible.

http://dx.doi.org/10.1016/j.tsf.2016.08.035
0040-6090/

Table 1
List of parameters of the CIGSe absorber layer for which a change was detected between conditioning states DA and LS.

Parameter	DA	LS
Doping concentration, measured N_A (10^{16} cm^{-3})	0.38	4.9
Peak energy of trap 1, $E_C - E_{T1}$ (meV)	119	94
Peak energy of trap 2, $E_C - E_{T2}$ (meV)	227	227
Standard deviation, energy of trap 1, σ^E_{T1} (meV)	16.2	17.7
Standard deviation, energy of trap 2, σ^E_{T2} (meV)	50	50
Peak concentration of trap 1, N_{T1} (10^{16} eV^{-1} cm^{-3})	1.1	3.16
Peak concentration of trap 2, N_{T2} (10^{16} eV^{-1} cm^{-3})	0.1	0.1
Electron capture cross section of trap 1, $\sigma_{T1,n}$ (10^{-14} cm^2)	1	1
Electron capture cross section of trap 2, $\sigma_{T2,n}$ (10^{-14} cm^2)	3	3
Hole capture cross section of trap 1, $\sigma_{T1,p}$ (10^{-18} cm^2)	1	1
Hole capture cross section of trap 2, $\sigma_{T2,p}$ (10^{-18} cm^2)	1	1

For all samples, doping concentration N_A was obtained from capacitance-voltage measurements. Two characteristic trap states with a Gaussian energy distribution (T1, T2), were detected by admittance spectroscopy. From these measurements the main parameters of the traps, like peak defect concentration N_{T1} and N_{T2}, activation energy E_{T1} and E_{T2}, and the standard deviation of their energy distribution σ^E_{T1} and σ^E_{T2} were extracted. Table 1 contains all parameters of the CIGSe absorber layer for which a change between conditioning states (DA and LS) was detected by capacitance-voltage measurements and admittance spectroscopy, or in the case of capture cross sections via simulation.

TRPL decays were measured after chemical etching with a 5% acetic acid solution to dissolve the i-ZnO and ZnO:Al window layers, leaving only the CdS buffer layer and the CIGSe absorber layer. A dye laser system with a peak excitation wavelength of 650 nm, a repetition rate of 2 MHz and a pulse duration of 7 ps at full width half maximum (FWHM) was used for excitation. Detection of the photoluminescence was done with the time correlated single photon counting technique at a wavelength corresponding to the maximum of the PL spectra of the samples ($\lambda = 1050$ nm). Laser power was varied by neutral density filters and measurements were carried out for an average power $\overline{P} =$ 0.5, 1, 2 and 7 mW. For these conditions the density of excited charge carriers Δn can be expressed in multiples of the doping density used in simulations N_A. In the LS state Δn then ranges from $0.5 \cdot N_A$ to $7 \cdot N_A$, while in the DA state Δn ranges from $6 \cdot N_A$ to $85 \cdot N_A$. The laser excitation spot on the sample was measured to have an area of $A = 0.2$ mm^2 at FWHM.

2.2. Simulation

A one dimensional model was used for the simulations using Synopsys TCAD (version J-2014.09-SP1, published by Synopsys Inc., 2014). The simulation was done for room temperature ($T = 300$ K) for open circuit conditions. For each time step the transient simulation calculates optical generation and recombination rates for each recombination mechanism included in the model, as well as solving the Poisson and continuity equations for electrons and holes. The charge carrier concentrations in the valence band p and conduction band n were calculated using the Boltzmann approximation, allowing to calculate an effective density of states for each band, as can be found in Table 2. For this work n and p will refer to the electron and hole concentrations respectively as a function of position and time. It must be kept in mind that charge carrier concentrations as well as recombination rates are calculated for each knot in the mesh and each time step, with the exception of the interface recombination, which happens only at one position and is therefore only a function of time. Likewise n_0 and p_0 refer to the electron and hole concentrations in equilibrium, in this case as a function of position.

A total of 200 ns are simulated, including the duration of the pulse, which is set to arrive at a simulation time of 10 ns. The minimal time step, which is used during the duration of the pulse, is of 0.2 ps. For later times, the time steps increase slowly and reach a maximum of 0.1 ns. A meshing procedure of the individual layers allows to solve the equations for each knot along the 1-D axis of the simulation. The meshing is set to be finer near the interfaces between layers or outer surfaces of the layers, while getting less refined towards the middle of each layer. The minimal step is of 0.01 nm and the maximum step is of 0.98 nm.

Table 2
Further parameters for simulation of TRPL decay. For the band gap E_g of the CIGSSe absorber, there is a linear increase from front (f) to back (b). The same is true for the absorption coefficient α. The doping concentration N_A of the absorber layer varies between conditioning states DA and LS.

Simulation parameter	CdS	CIGSe
Thickness d (μm)	0.065	1.92
Electron affinity χ (eV)	4.27	4.34(f)
Band gap E_g (eV)	2.4	1.18 (f)… 1.36 (b)
Absorption coefficient α at $\lambda = 650$ nm (μm^{-1})	1	2.91 (f)… 3.15 (b)
Doping concentration, simulation N_A (10^{16} cm^{-3})	50	0.26 (DA)… 3.0 (LS)
Electron mobility μ_n (cm^2 V^{-1} s^{-1})	100	60
Hole mobility μ_p (cm^2 V^{-1} s^{-1})	25	5
Effective density of states cond. band N_C (10^{18} cm^{-3})	2.2	2.2
Effective density of states val. band N_V (10^{18} cm^{-3})	18	18
Radiative recombination constant B_{rad} (10^{-9} cm^3 s^{-1})	–	2
Interface recombination velocity S_0 (10^4 cm s^{-1})	1	

Excitation is simulated by a single laser pulse with wavelength $\lambda =$ 650 nm, a Gaussian pulse time profile and a FWHM duration of 7 ps. The peak intensity of the laser pulse I_0 is calculated so that the integrated energy of a single pulse E_{pulse} multiplied by the repetition rate of the laser ($f = 2$ MHz) matches with the measured average output power of the laser $\overline{P}$. The simulation was carried out for different values of $\overline{P}$ to match the experiments.

2.3. Charge carrier dynamics

Fig. 1 contains a band diagram of the CIGSe absorber layer and schematically shows the recombination, capture and emission mechanisms taken into account in our model, which we will now shortly present. Table 2 contains a list of simulation parameters that play a role for the charge carrier dynamics in both the CdS and CIGSe layers.

The radiative recombination rate R_{rad} is given by Eq. (1) where B_{rad} is the radiative recombination constant.

$$R_{rad} = B_{rad}\,(p\,n - p_0\,n_0) \tag{1}$$

R_{rad} represents the main result of the simulation, since it is used to calculate the total radiative recombination intensity for each time

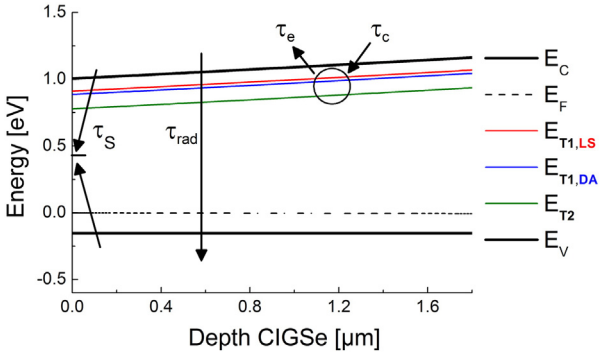

Fig. 1. Band diagram of CIGSe absorber layer with energies of the conduction band E_C, valence band E_V and Fermi level in equilibrium E_F. Times τ_e and τ_c stand for the minority carrier lifetimes for emission and capture to and from trap states with energies $E_{T1,LS}$ for the light soaked samples, $E_{T1,DA}$ for the dark annealed sample and E_{T2}. Radiative recombination takes place in the entire absorber layer, with a lifetime τ_{rad}, while interface recombination happens at the front surface with a lifetime τ_S.

Please cite this article as: J.F.L. Salas, et al., Simulation of metastable changes in time resolved photoluminescence of Cu(In,Ga)Se2 thin film solar cells upon light soaking treat..., Thin Solid Films (2016), http://dx.doi.org/10.1016/j.tsf.2016.08.035