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Light-induced changes in the minority carrier diffusion length of Cu(In,Ga)Se_2 absorber material

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ABSTRACT

In this study strong evidence for an illumination-induced change in minority charge carrier diffusion length is given for Cu(In,Ga)Se_2 solar cells. After annealing under illumination (light soaking) the cells show the well-known metastable increase in open circuit voltage, but also a metastable reduction in current collection efficiency (which can be reversed by annealing in the dark). Partly, this can be attributed to an increase in doping density causing a reduced space charge region width as verified by capacitance-voltage profiling. Nevertheless, by using time-resolved photoluminescence and electron-beam-induced current measurements we found that the changes in doping density and space charge region width are not sufficient to describe the modification in current collection efficiency. Additionally there seems to be a reduction in minority carrier diffusion length and lifetime after white light soaking. This can be explained by a metastable change of electronic defects as found in temperature-dependent admittance spectroscopy. Device simulations confirm the impact of the found defects on the photocurrent.

1. Introduction

Thin film solar cells based on Cu(In,Ga)Se_2 (CIGSe) exhibit a series of metastable effects which can noticeably influence the solar energy conversion [1]. One such common observation in CIGSe solar cells is their metastable behavior under illumination. For example, upon white light soaking (LS), i.e. air-annealing under illumination, an increase of the open circuit voltage V_{oc} can be observed [2–4] which leads to an improvement of the device performance, while in most cases air-annealing in the dark (DA) reverses this effect. This phenomenon has been attributed to an increase in apparent doping density N_A upon light soaking [5,6], as observed in capacitance-voltage profiling measurements. However, additionally to the metastable change in V_{oc} we also observe a metastable effect on the current collection efficiency which cannot be explained by only a change in N_A. In this work we investigate this effect comprehensively by means of time-resolved photoluminescence (TRPL) and electron-beam-induced current (EBIC) measurements, defect spectroscopy (TAS) and device simulations, thereby revealing the possible role of (native) defects which may act as electron traps or recombination centers and thus limit the minority carrier lifetime and diffusion length.

2. Methods

2.1. Sample conditioning

The investigated samples were derived from a 10×10 cm^2 segment of a standard glass/Mo/Cu(In,Ga)Se_2/CdS/i-ZnO/ZnO:Al solar cell. Its absorber was grown by a co-evaporation multistage process and had an integral composition of 22 at.-% copper, a Ga/(Ga+In) ratio of 0.34 [7], and a thickness of about 1.9 µm. CdS served as a buffer layer and i-ZnO/ZnO:Al as the transparent conducting oxide (TCO). The absorber had a linear band gap grading as derived from glow discharge optical emission spectra (GDOES, SPECTRUMA ANALYTIC). More details about the processing can be found in [8]. The original sample was cut into smaller pieces for the different experiments. For electronic characterization complete devices with a Ni/Al/Ni contact grid were used. For TRPL measurements the TCO layer was removed by chemical etching with a 5% solution of acetic acid, since otherwise the PL decay would be dominated by separation of charge carriers due to strong internal fields at the heterojunction [9]. The CdS layer was left in place as a protective cover because bare CIGSe films may degenerate very quickly upon air exposure [10].

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Two metastable states were created by long-term thermal storage at T=90 °C: All samples were annealed in the dark for 15 h (referred to as "DA state" in the following). Some samples were additionally annealed under simulated AM1.5 illumination for 9 h (referred to as "LS state").[2] The annealing and light soaking steps were performed in ambient atmosphere on a Torrey Pines Scientific heating stage controlled by a temperature controller using a Pt100 sensor mounted on the surface of an identical dummy sample placed next to the device under treatment and utilizing a solar simulator. All measurements were carried out within a few hours after the treatment. Supplementary measurements in our labs showed that both the sample conditioning as well as the results of the experiments shown in this paper were well reproducible.

2.2. Experimental details

Current-voltage (JV) characteristics were measured under standard test conditions (STC).

Capacitance-voltage (CV) measurements were performed at room-temperature in dark ambiance under 4-point probe geometry with a HP4194A impedance analyzer within a bias range of (− 0.5…0.5) V, an alternating voltage with an amplitude of 30 mV and a measurement frequency of 100 kHz. To obtain the space charge region width W_{scr} and the net doping concentration N_A a static dielectric constant of $\varepsilon = 13.6$ [9] was assumed in the Mott-Schottky analysis.

Internal quantum efficiency (IQE) was obtained by measuring external quantum efficiency (EQE) and optical reflection with a Bentham PVE300 spectrometric QE-system (using an integrating sphere for the reflection measurements).

Temperature-dependent admittance spectroscopy (TAS) was carried out on the complete solar cell in a closed cycle He cryostat under vacuum in the temperature range between 30 K and 300 K in 2 K steps. A Solartron 1260A gain phase impedance analyzer was used for sweeping between frequencies of 10 Hz and 1 MHz with an amplitude of 30 mV.

Room-temperature PL decay curves were measured by the time-correlated single-photon counting technique (TCSPC). Photo excitation was provided by a dye laser-system emitting at 650 nm with a repetition rate of 2 MHz, a maximum photon flux density of 7×10^{11} cm^{-2} (averaged energy per pulse: 5 nJ) and a pulse width of 7 ps. Pulse broadening due to optical and electronic components was approximately 200 ps. Excitation took place under an angle of 45° on an elliptical beam area of 3 mm^2. The PL was detected with a NIR PMT Module of Hamamatsu (H10330A-75 Series). The time-correlated statistical evaluation was provided by a single photon counting module (SPC 130) by Becker & Hickl. The average laser power $\overline{P}$ was set to 0.5 mW in the LS case and 7 mW in the DA case. It was tuned such that the density ρ (=Δn, Δp) of injected electron-hole pairs roughly matched the doping density N_A of the respective sample, so that a relative injection level of $\rho/N_A \approx 1$ was reached. The density of injected electron-hole pairs ρ was estimated as being equal to the density of injected photons which was calculated using the above mentioned excitation parameters and assuming a penetration depth of 120 nm. For the measurements reported here, the monochromator was tuned to the PL peak, which occurred at λ_{PL} = 1050 nm (E_{PL} = 1.18 eV) with a resolution of 15 nm due to monochromator output slit width.

Junction-EBIC measurements were conducted at different positions on a cross section of a CIGSe sample in a FEI Helios Nanolab SEM system applying an acceleration voltage of 5 kV and an electron current of 0.17 nA. Care was taken to expose the sample as little as possible to the electron beam before the actual measurement (less than 10 s at a given magnification) in order to minimize its effect on the metastable LS or DA conditions.

[2] Previous investigations of the metastable behavior on this sample type had suggested sufficient saturation of the LS and DA effect after the given times.

Table 1
Device parameters of investigated thin film solar cells in the light-soaked (LS) and dark-annealed (DA) state as measured by CV, JV, IQE and TAS.

	DA	LS
Net doping density, N_A (10^{16} cm^{-3})	0.38	4.90
Space-charge region width, W_{scr} (nm)	424	152
Built-in potential, V_{bi} (mV)	519	864
Short-circuit current density (from IQE with light bias), $j_{sc,IQE}$ (mA/cm^2)	31.1	30.7
Open circuit voltage, V_{oc} (mV)	702	730
Fill factor, FF (%)	79.7	80.2
Efficiency, η (%)	17.4	18.0
Saturation current density, J_0 (nA/cm^2)	399	128
Ideality factor, n_{ideal}	1.51	1.47
Defect #1: Density, $N_{t,1}$ (10^{15} cm^{-3})	0.45	1.40
Defect #1: Activation energy, $E_{a,1}$ (meV)	119	94
Defect #1: Attempt-to-escape frequency, $\xi_{0,1}$ (kHz)	77	7.7
Defect #2: Density, $N_{t,2}$ (10^{15} cm^{-3})	8.1	–
Defect #2: Activation energy, $E_{a,2}$ (meV)	227	–
Defect #2: Attempt-to-escape frequency, $\xi_{0,2}$ (kHz)	88	–

3. Results

3.1. Basic characterization

The device parameters extracted from the JV and CV measurements are listed in Table 1. Upon light soaking we see an increase in the open circuit voltage of ΔV_{oc} = 28 mV. The inspection of the CV data for both states reveals that the net doping concentration N_A is about an order of magnitude larger for the LS state (N_A^{LS}/N_A^{DA} = 12.9). The enhancement of the doping concentration leads to a narrowing of the space charge region of $\Delta W_{scr} \approx -270$ nm.

Furthermore we found a reduced infrared-light response in the quantum efficiency upon light soaking: Fig. 1 shows the IQE spectra for both the LS and the DA state, each measured with and without white light bias. A clear difference in the spectra is seen in the wavelength range between 650 nm and 1000 nm which — upon integrating the spectra and considering the AM1.5g spectrum — leads to a slightly reduced short circuit current density $j_{sc,IQE}$ for the light soaked state. This effect is more pronounced when measuring without light bias ($\Delta j_{sc,IQE}$(no bias) = − 0.7 mA/cm^2) than when measuring with light bias ($\Delta j_{sc,IQE}$(bias) = − 0.4 mA/cm^2). An analysis of the PL spectra in the LS and DA state (not shown) reveals identical absorption spectra for the two states. Thus differences in the IQE spectra indicate differences in the collection efficiency. According to the Gärtner model [11] it can be

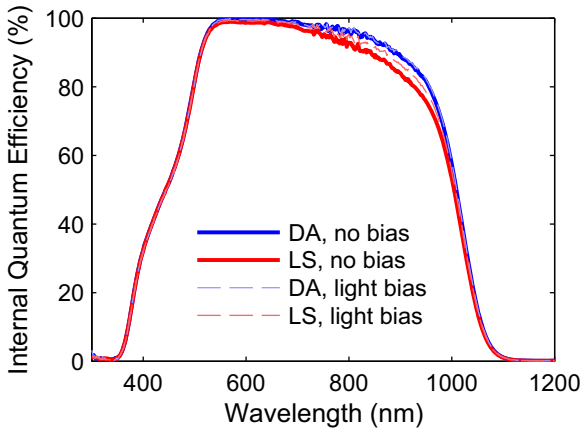

Fig. 1. Internal quantum efficiency for both states DA (blue) and LS (red) measured without bias (solid lines) and with white light bias (dotted lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)