NANOSYSTEMS:
PHYSICS, CHEMISTRY, MATHEMATICS

Kabulov R.R., et al. *Nanosystems: Phys. Chem. Math.*, 2023, **14** (1), 127–131.
http://nanojournal.ifmo.ru
DOI 10.17586/2220-8054-2023-14-1-127-131

Original article

Time of transition processes in a CdS-CIGS structural solar cells in the short-wave part of the absorption spectrum at different loading resistances

Rustam R. Kabulov[1,a], Farrux A. Akbarov[2,1,b], Anvar A. Alimov[2,c]

[1]Physical – Technical Institute Academy of Sciences of the Republic of Uzbekistan, Tashkent, Uzbekistan
[2]Tashkent State Technical University named after Islam Karimov, Tashkent, Uzbekistan

[a]krr1982@bk.ru, [b]farrux1927@mail.ru, [c]alimovanvar62@gmail.com

Corresponding author: F. A. Akbarov, farrux1927@mail.ru

ABSTRACT The work is devoted to the study of the influence of solar radiation in the short-wave part of the absorption spectrum at different loading resistances on the lifetime (τ) of minority photogenerated charge carriers (Δn) of a thin-film solar cell based on Cu(In,Ga)Se_2. It was found that with an increase in the generated photocurrent and the magnitude of the load resistance the lifetime of minority photogenerated charge carriers of a thin-film solar cell based on Cu(In,Ga)Se_2 increases. The obtained experimental results are interpreted by the charge exchange of defect states, which capture the injected and photogenerated electrons, as a result of which they cease to be active recombination centers.

KEYWORDS CIGS, solar cell, monochromatic radiation, absorption coefficient, lifetime, photogenerated charge carriers, minority charge carriers.

ACKNOWLEDGEMENTS The authors express their gratitude to the management, employees of the Physical-technical Institute Academy of Science of the Republic of Uzbekistan for technical assistance in performing experimental research, discussing the results of these scientific studies and writing an article, and also express their gratitude to the employees of the Tashkent State Technical University who took an active part in discussing the results of our scientific research.

FOR CITATION Kabulov R.R., Akbarov F.A., Alimov A.A. Time of transition processes in a CdS-CIGS structural solar cells in the short-wave part of the absorption spectrum at different loading resistances. *Nanosystems: Phys. Chem. Math.*, 2023, **14** (1), 127–131.

1. Introduction

One of the important parameters that determine the efficiency of photosensitive structures is the lifetime (τ) of minority photogenerated charge carriers (Δn). In real solar cells and photodetectors, due to the complexity of the structure design, since in the process of creating a photoactive CIGS layer, due to the mutual diffusion of chemical elements from the CdS and CIGS layers, a layer that is inhomogeneous in respect to chemical composition is formed at the CdS/CIGS heterojunction boundary in the photoactive layer. In the photovoltaic mode, the photovoltage on the load resistance is connected in the direct direction to the p-n junction, it changes both the size of the space charge region and the distribution of the internal potential. In this regard, it was interesting to establish the effect of the load resistance on the lifetime of nonequilibrium charge carriers when illuminated with short-wavelength solar radiation, which is mainly absorbed near the heterojunction ($\lambda_1 \approx 450$ nm, $hv_1 \approx 2.76$ eV and $\lambda_2 \approx 520$ nm, $hv_2 \approx 2.40$ eV).

Studying the relaxation characteristics of photosensitive structures, such as photocurrent decay (J_{ph}), under illumination with discontinuous monochromatic light, will allow one to estimate the value of τ and establish the mechanism of photogeneration of nonequilibrium photogenerated charge carriers and the processes of their recombination under illumination. It is known that the magnitude of the photocurrent depends on the concentration of photogenerated charge carriers – Δn [1]. The time characteristic Δn is determined by relation (1) [1]:

$$\frac{d(\Delta n)}{dt} = -\frac{\Delta n}{\tau}, \tag{1}$$

where, τ is the lifetime of photogenerated charge carriers. The solution to equation (1) has the form (2),

$$\Delta n = \Delta n(0) \cdot \exp(-t/\tau), \tag{2}$$

where $\Delta n(0)$ is the stationary maximum value of photogenerated charge carriers. For the experimental determination of τ, it is necessary to plot the time dependence of the photocurrent value on a logarithmic scale ($\ln(J_{ph})$ on t), where the slope of the obtained straight line gives one the value of τ for Δn in the photoelectric converter.

2. Experimental details

To study the effect of the resistance value of the external load (R_{load}) on τ Δn under illumination with monochromatic radiation of the short-wavelength absorption spectrum ($\lambda_1 = 450$ nm, $hv_1 \approx 2.76$ eV and $\lambda_2 = 520$ nm, $hv_2 \approx 2.40$ eV), a heterostructural solar cell was created with a photosensitive region of polycrystalline indium gallium-copper selenide ($Cu(In,Ga)Se_2$ – CIGS), $E_g \approx 1.30 \pm 0.03$ eV, $T = 300$ K) [2]. Since thin-film CIGS solar cells are widely used in the creation of photovoltaic structures for various purposes [3], these studies are important.

In the process of creating photoconverters with the CdS/CIGS structure, due to the mutual diffusion of chemical elements from the CdS and CIGS layers, at the interface of the CdS/CIGS heterojunction in the photoactive CIGS layer, layers that are inhomogeneous in chemical composition are formed, which can lead to the formation of defect states. Defect states reduce the lifetime of photogenerated nonequilibrium carriers. In photovoltaic mode, the voltage across the load resistor (U_L) is connected in the forward direction to the p-n junction. U_L changes the size of the space charge region and the distribution of the internal potential of the structure. In this regard, it was interesting to establish the effect of the load resistance on the lifetime of nonequilibrium charge carriers when illuminated with short-wavelength solar radiation, which is mainly absorbed near the heterojunction ($\lambda_1 \approx 450$ nm, $hv_1 \approx 2.76$ eV and $\lambda_2 \approx 520$ nm, $hv_2 \approx 2.40$ eV). Since, under illumination with λ_1 ($hv_1 \approx 2.76$ eV) due to partial absorption of quanta in the CdS layer, the number of quanta generating electron-hole pairs in the photoactive CIGS layer is less than under illumination with λ_2, $hv_2 \approx 2.40$ eV, as a result, the photocurrent is of little value.

For research, photosensitive SnO_2/n-CdS/p-CIGS/Mo heterojunction structures were fabricated, in which n-CdS layers ($E_g = 2.44$ eV, $T = 300$ K) were used as the front buffer layer, which were deposited on the p layer. -CIGS by vacuum thermal spraying from the original source of CdS. The SnO_2 layers served as a frontal transparent conducting layer and were created by DC ion magnetron sputtering of a tin target in an argon and oxygen atmosphere [3, 4]. As mentioned above, the base material for the solar cell was p-type polycrystalline CIGS films grown by the method of simultaneous thermal evaporation in vacuum from initial sources of Cu, In, Ga, and Se on the surface of molybdenum (Mo) [5]. The rear electrical contact was $Mo_{0.5}$ μm thick, which was deposited by DC magnetron ion sputtering in an argon atmosphere from a Mo target onto the surface of a glass substrate 1 mm thick. The upper collecting electrical contact for collecting photogenerated nonequilibrium electrons was created from metallic silver (Ag) and indium (In), which was deposited on the surface of the SnO_2 layer by vacuum thermal spraying in the form of a comb.

Figure 1 shows the design of the created SnO_2-n-CdS/p-CIGS-Mo structural solar cell and the dimensions of the layers. The photocurrent generation process proceeds as follows: electromagnetic radiation quanta, passing through layers of transparently conducting SnO_2 and an n-CdS buffer layer, enter the photoactive region of CIGS, where nonequilibrium electron-hole pairs are absorbed and generated. In the case of $\lambda_2 \approx 520$ nm ($hv_2 \approx 2.40$ eV), the photocurrent is $\approx 30\%$ higher than in the case of $\lambda_1 \approx 450$ nm ($hv_1 \approx 2.76$ eV) ($J_{sc.green}/J_{sc.blue} \approx 1.3$). This is due to the fact that when quanta with $\lambda_1 \approx 450$ nm ($hv_1 \approx 2.76$ eV) are absorbed by the n-CdS layer ($E_g = 2.44$ eV), fewer λ_1 quanta participate in the photogeneration of nonequilibrium carriers into the photoactive CIGS layer. Accordingly, the total number of generated non-equilibrium electron-hole pairs into the photoactive CIGS layer will be less. The front In/Ag metal contact and the back Mo serve as electrical collecting electrodes.

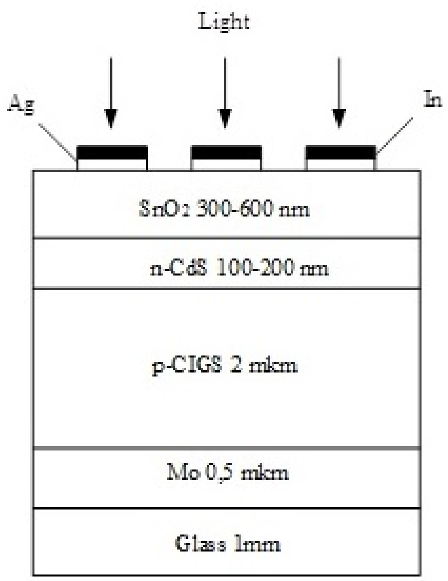

FIG. 1. Construction of the created SnO_2-n-CdS/p-CIGS-Mo structural solar cell

Figure 2 shows a schematic diagram of the installation for determining time of life for the photogeneration of nonequilibrium carriers – τ into the photoactive CIGS layer. The load resistance R_{load} and digital storage oscillograph (DO) connected in parallel with the SnO_2-n-CdS/p-CIGS-Mo structural solar cell.

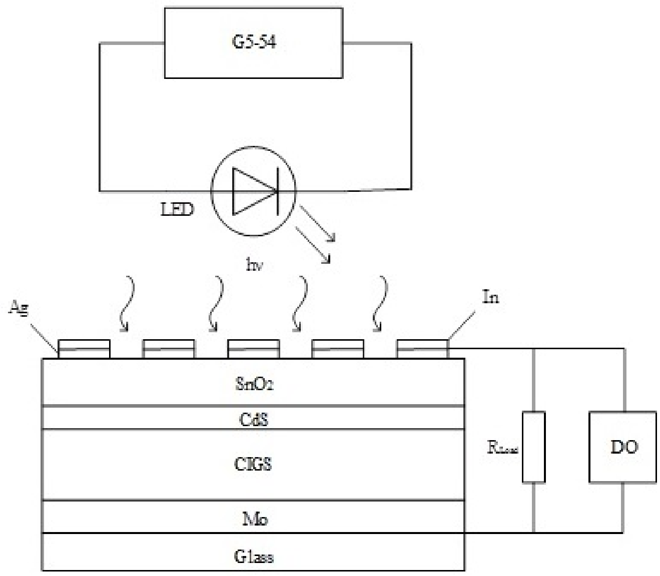

FIG. 2. Schematic diagram of the installation for determining τ

As a source of modulating electromagnetic radiation, we used light emitting diodes (LED) of green and blue radiation with a power of $\sim$ 40 mW. A voltage of 4 V, duration of 200 μs, and frequency of 1 kHz was applied to the LEDs from the G5-54 rectangular pulse generator. From the load resistance R_{load}, the alternating signal was fed to the input of the RIGOL 1102E digital storage oscillograph (DO).

3. Results and discussions

Figure 3 shows the results of relaxation curves of photogenerated currents, built on a logarithmic scale, recorded from load resistances of various values (from 800 Ohm to 100 kOhm and open circuit voltage ($R_{load} \approx$ 1 MOhm)) with a DO under illumination with light $\lambda_2 \approx$ 520 nm. Plotting the relaxation values of the photocurrent on a logarithmic scale shows that the experimental curves, in accordance with relation (2), can be described by a single exponent. From which it follows that one recombination center is involved in the relaxation process.

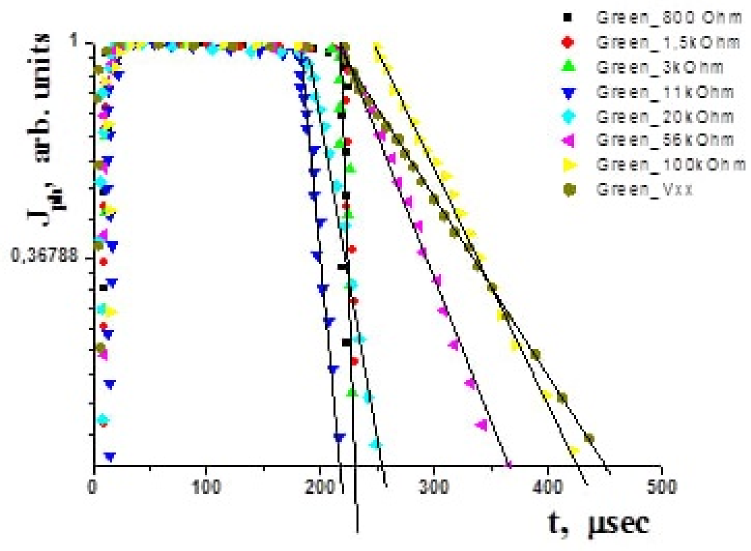

FIG. 3. Relaxation curves of photogenerated currents (J_{ph}), built on a logarithmic scale, taken from load resistances of various sizes (from 800 Ohm to 100 kOhm and no-load voltage (R_{load} ≈1 MΩ)) on a digital oscilloscope under illumination with radiation $\lambda_2 \approx$ 520 nm (green)

Figure 4 shows the experimental results of the dependence of $\tau\ \Delta n$ on R_{load}, determined in the SnO_2-n-CdS/p-CIGS-Mo structural solar cell, under illumination by monochromatic radiation of the blue and green spectrum with maxima at wavelengths $\lambda_1 \approx 450$ nm and $\lambda_2 \approx 520$ nm.

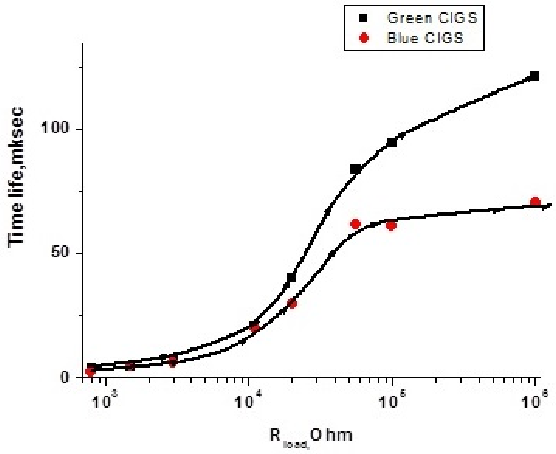

FIG. 4. Dependences of the lifetime Δn on R_{load} in the CdS-CIGS structure under illumination by monochromatic electromagnetic radiation with $\lambda_2 \approx 2520$ nm (green) and $\lambda_1 \approx 450$ nm (blue)

From the experimental results presented in Fig. 4, it follows that $\tau\ \Delta n$ in the range of R_{load} =800–1000 Ohm, in the CdS-CIGS heterostructure, has relatively high values $\tau\ \Delta n$ when the heterostructure illuminated with green light ($\lambda_2 \approx 520$ nm) than the blue light ($\lambda_1 \approx 450$ nm). Electromagnetic quanta with $\lambda_2 \approx 520$ nm ($hv_2 \approx 2.40$ eV) are weakly absorbed in the n-CdS layer ($E_g = 2.44$ eV), and are mainly absorbed in the Space Charge Region (SCR) area of the p-CIGS layer and partially in the quasineutral part, where absorption coefficient is high ($\sim 10^5$ sm^{-1}). As a result, nonequilibrium charge carriers are mainly photogenerated in the photoactive region of p-CIGS. Electromagnetic quanta with $\lambda_1 \approx 450$ nm ($hv_1 \approx 2.76$ eV) are absorbed in the n-CdS layer, absorbed in the SCR of the heterojunction, as well as in the p-CIGS photoactive layer. Since at $\lambda_1 \approx 450$ nm ($hv_1 \approx 2.76$ eV) relatively few quanta reach the photoactive quasineutral region of the p-CIGS layer, fewer non-equilibrium charge carriers are generated and a small value of the short-circuit current is obtained in relation to the case of $\lambda_2 \approx 520$ nm ($hv_2 \approx 2.40$ eV) ($J_{sc.green}/J_{sc.blue} \approx 1.3$).

Due to the difference in the lattice constants of the CdS and CIGS layers, surface states (N_{ss}) are formed at the heterojunction boundary, which will act as recombination centers for Δn. Concentration $N_{ss} \sim d^{-2}$ [6,7], where d is the distance between dislocations formed due to the mismatch of the crystal lattices of the contacting materials (3),

$$d = \frac{a_{CIGS}a_{CdS}}{a_{CIGS} - a_{CdS}}. \tag{3}$$

Taking into account the lattice constant of CdS and CIGS [8], the values of $d \approx 315$ Åand $N_{ss} = 1.96 \cdot 10^{10}$ sm^{-2} were calculated. Also, in the volume of the photoactive part of the p-CIGS layer, there are crystal lattice defects and uncontrollable impurities, which play the role of recombination centers (N_{rs}) for nonequilibrium photogenerated charge carriers. If the photogeneration of charge carriers mainly occur near recombination states, this leads to a decrease in τ Δn. However, under certain conditions, when these recombination centers can be neutralized, and they cease to play the role of recombination centers for Δn [9, 10]. The recharge of recombination centers [9, 10], due to the capture of the injected charge carrier can lead to the reactivation of these centers.

As mentioned above, in the n-CdS/p-CIGS heterostructure, $\tau\ \Delta n$ has relatively high values when its illuminated with light with $\lambda_2 \approx$520 nm than at $\lambda_1 \approx 450$ nm in the range of R_{load} =800–10^6 Ohm. This is due to the fact that under illumination with light with $\lambda_2 \approx 520$ nm, a large value of the short-circuit current (J_{sc}) is generated in the heterostructure in relation to the case of $\lambda_1 \approx 450$ nm ($J_{sc.green}/J_{sc.blue} \approx 1,3$). As a result, more voltage U_{load} falls on R_{load}. Voltage U_{load} is connected in the forward direction to the photodiode, and a relatively large dark injection current through the diode. The recombination centers, capturing the injected electrons, are recharged and cease to be active recombination centers. In the case of illumination with light with $\lambda_2 \approx 2520$ nm, there are more photogenerated electrons, and more N_{rs} centers are inactive, which should lead to an increase in $\tau\ \Delta n$.

It can be seen from Fig. 4 that $\tau\ \Delta n$ both for the case of illumination with $\lambda_1 \approx$450 nm and for the case of illumination with $\lambda_2 \approx 520$ nm grows to a value of $R_{load} = 50$ kOhm and further with an increase in R_{load} the growth of τ Δn slows down. This is due to the fact that with an increase in R_{load}, the effective current through R_{load} and the heterostructure decreases, which leads to a partial recharge of N_{rs} centers, as a result of which, some of the N_{rs} centers again become recombination active.

4. Conclusion

The study of the influence of the load value and the power of monochromatic radiation in the short-wavelength part of the electromagnetic radiation spectrum showed that the lifetime of non-equilibrium carriers increases with an increase in the load resistance and illumination intensity, that is, either with an increase in the injection current and photogenerated carriers. The lifetime of nonequilibrium carriers decreases with an increase in the absorption coefficient of radiation, which is absorbed more near the heterojunction. The observed effect is associated with a decrease in recombination centers in the photoactive part of the heterojunction as a result of the recharging of defect states in the p-CIGS layer.

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Submitted 20 October 2021; revised 27 July 2022, 13 December 2022; accepted 1 February 2023

Information about the authors:

R. R. Kabulov – Physical-Technical Institute Academy of Sciences of the Republic of Uzbekistan, 2 “B”, Ch. Aytmatov str., Tashkent, 100084, Uzbekistan; ORCID 0000-0003-3157-9038; krr1982@bk.ru

F. A. Akbarov – Physical-Technical Institute Academy of Sciences of the Republic of Uzbekistan, 2 “B”, Ch. Aytmatov str., Tashkent, 100084, Uzbekistan; Tashkent State Technical University named after Islam Karimov, 2A, University str. Tashkent, 100095, Uzbekistan; ORCID 0000-0003-0045-9201; farrux1927@mail.ru

A. A. Alimov – Tashkent State Technical University named after Islam Karimov, 2A, University str. Tashkent, 100095, Uzbekistan; ORCID 0000-0002-0048-3175; alimovanvar62@gmail.com

Conflict of interest: the authors declare no conflict of interest.