PROCEEDINGS OF THE INTERNATIONAL CONFERENCE
NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **3** No 2, 02NEA06(4pp) (2014)

Recombination Losses in Solar Cells Based on n-ZnS(n-CdS) / p-CdTe Heterojunctions

O.A. Dobrozhan*, A.S. Opanasyuk, V.F. Nefedchenko

Sumy State University, 2, Rymskogo-Korsakova Str., 40007 Sumy, Ukraine

(Received 03 July 2014; published online 29 August 2014)

The recombination losses in ancillary and absorber layers of solar cells based on *n*-ZnS / *p*-CdTe and *n*-CdS / *p*-CdTe heterojunctions with ITO and ZnO current-collecting frontal contacts were calculated. The effect of recombination losses in solar cells with structure ITO(ZnO) / CdS(ZnS) / CdTe on the short-circuit current (J_{sc}) and the efficiency (η) of photovoltaic devices at different window layer thickness CdS (ZnS) (50-300 nm) and at invariable of current-collecting layer thickness (200 nm) were investigated. The influence of recombination velocity ($S = 10^7$-10^9 cm/s) on the main features of solar cells was researched. It was established that solar cells with structure ZnO/ZnS/CdTe at the concentration of uncompensated acceptors in absorber layer ($N_a - N_d$) = 10^{15}-10^{17} cm^{-3} and at window layer thickness 50 nm at recombination velocity $S = 10^7$ cm/s have the highest efficiency values (15.9-16.1 %).

Keywords: Solar cells, Recombination losses, Efficiency, ZnS / CdTe, CdS / CdTe.

PACS numbers: 84.60.Jt, 73.61.Ga

1. INTRODUCTION

One of the ways out of the mankind from the existing global energy crisis is massive use of photovoltaic cells to convert solar energy into electrical energy. Currently, the most common used solar cells (SC) are based on silicon technology. The alternative to this converters are thin film solar cells based on the *n*-CdS / *p*-CdTe heterojunction (HJ). It should be noted that this is the first technology that has allowed to reduce the cost of production of solar energy to 0.57 $/Watt, which is lower than the economically justified price of solar energy in $1/Watt [1].

The maximum theoretical efficiency of thin film SC with absorber layer CdTe is 28-30 % [2]. However, the real efficiency of solar cells on the basis of *n*-CdS / *p*-CdTe HJs with "superstrate" structure nowadays is 20.4 % [3], and the efficiency of solar modules with an area of more than 1 cm^2 – 16.5 % [4, 5]. The difference between the theoretical predictions and the actual values of the efficiency of the devices is explained by optical, electrical and recombination losses in the conversion of solar energy into electricity.

Further increasing of the efficiency of the SC is only possible if minimizing these losses, optimizing their design and improving properties of the individual layers.

In the "superstrate" structure of SC with *n*-CdS / *p*-CdTe HJ ITO ($(In_2O_3)_{0.9}$-$(SnO_2)_{0.1}$) or FTO (SnO_2:F) [6, 7] was traditionally used as economically sublayer. However, in recent times, zinc oxide films doped with aluminum (ZnO:Al) began to be used as the front of conductive layers photovoltaic devices [8, 9]. This material is cheaper than ITO or FTO and does not contain not common and costly elements which, for example, include the indium.

It should be noted that in the production of thin film solar cells play an important role in the choice of window layer. Currently, as widely used CdS ($E_g = 2.42$ eV). Alternative CdS films can be ZnS thin layers that have already found application in solar cell-based compounds CIS, CIGS, CZTSe and CZTS [10, 11]. Zinc sulphide has a substantially larger width of the band gap ($E_g = 3.68$ eV) than the cadmium sulfide, which allows to extend the range of photosensitivity of relevant SC and to increase their short-circuit current [12]. This compound is non-toxic due to the absence of heavy metals. Finally, ZnS layer may be an antireflection coverage that increases the number of photons absorbed by solar cells and therefore its efficiency [13].

The authors of papers [14, 15] considered recombination losses of photogenerated carriers in SC with the structure of glass / ITO(TCO) / CdS / CdTe /back metal contact. But the influence of the recombination losses on the efficiency of SC with new structure glass / ZnO / ZnS / CdTe / back metal contact at the moment is not investigated. This caused the purpose of the study. Note that the calculations of recombination losses in solar cells in this work were executed with respect to optical losses of the light we found earlier in [16].

The main aim of this work is the calculation and comparison of recombination losses in solar cells with two different structures, the study of their influence on the efficiency of a solar cell on the base of *n*-ZnS / *p*-CdTe and *n*-CdS / *p*-CdTe HJs with front conductive contacts: ITO and ZnO.

2. DETERMINING WIDTH OF THE SPACE CHARGE REGION AND QUANTUM YIELD OF SOLAR CELLS

Thin film SC-based on «superstrate» HJ type have a multilayer structure and contain substrate (glass) window (CdS, ZnS) and absorber (CdTe) layers, conductive front (ITO, ZnO) and metal back contact. Schematic diagram of a typical photovoltaic design with the structure of glass / ITO(ZnO) / CdS(ZnS) / CdTe / back contact are presented in [16].

One of the important parameters that determine the efficiency of photoelectric conversion of light and is used to analyze recombination losses in SC is the width

---

[*] dobrozhan.a@ukr.net

of space charge region (*d*), in other words, the depletion region that occurs at the contact of heteropair. This width is mainly dependent on the concentration of uncompensated acceptors $(N_a\text{-}N_d)$ (i.e., the difference between the concentration of acceptors and donors) that are in the material. Because of the high doping level of the window and high conductivity of cadmium sulfide (10^{17}-10^{18} cm^{-3}) and zinc oxide (10^{17} cm^{-3}) doped films the depletion region *n*-CdS(*n*-ZnS) / *p*-CdTe HJ is situated in CdTe layer. Thus, the processes of-charge transfer that take place in the depletion HJ from a physical point of view is similar to those that occur in areas of depletion region of Schottky diode. In this case, the width of the space charge region can be found by using the expression [2]:

$$d = \sqrt{\frac{2\varepsilon\varepsilon_0 \;\; \varphi_0 - qU}{q^2 \;\; N_a - N_d}}\,, \tag{1}$$

where, ε – relative dielectrically permittivity of the material; ε_0 – permittivity of vacuum; φ_0 – barrier height on HJ; U – applied external voltage; q - electron charge; $(N_a - N_d)$ – the concentration of uncompensated acceptors in the absorbing layer.

In this paper for the calculation values which are presented in Table 1 were used.

Calculation of the width of the space charge region makes it possible to determine the quantum yield (Q) SC *n*-CdS(*n*-ZnS) / *p*-CdTe by the following formula [17]:

$$Q = \frac{1 + \dfrac{S}{D_P}\left(\alpha + \dfrac{2\cdot \;\; \varphi_0 - qU}{dkT}\right)^{-1}}{1 + \dfrac{S}{D_P}\left(\dfrac{2\cdot \;\; \varphi_0 - qU}{dkT}\right)^{-1}} - \frac{e^{-\alpha d}}{1 + \alpha L_n}\,, \tag{2}$$

where, S – recombination velocity for heterojunction interface; D_n, D_p – diffusion coefficients of holes; α – coefficient of light absorption in a layer of CdTe; k – Boltzmann constant; T – temperature; L_n – diffusion length of electrons ($L_n = \;\tau_n \cdot D_n\;^{1/2}$ where τ_n – the lifetime of electrons).

The value of the coefficient of light absorption in CdTe for a range of wavelengths (300-850) nm was taken by us from [18].

It should be noted that the expression (2) does not account for recombination on the back surface of CdTe layer, which can lead to significant losses of converter efficiency in case of little band gap.

Table 1 – Main parameters, used for *d* and *Q* definition

Parameter	Value
ε	10,6
$\varphi_0 - qU$	(0,70 eV)$_{\text{CdS}}$, (0,82 eV)$_{\text{ZnS}}$
$(N_a - N_d)$	10^{11}-10^{17} cm^{-3}
S	10^7-10^9 cm/s
τ_n	10^{-9} s
D_n	25 cm^2/s
D_p	2 cm^2/s
T	300 K

If we neglect the second term of the expression (2) (as a result of strong absorption light flux at small wavelengths), as well as while absence of recombination of charge carriers at the surface ($S = 0$), the values of the quantum yield can reach 1. That's why, the deviation of obtained values Q from maximal at a λ = (300-850) nm wavelength can be explained by surface recombination.

Fig. 1 shows a graph of the photoelectric quantum yield on the concentration of uncompensated acceptors $(N_a - N_d)$ and recombination velocity (S) of carriers on the interface of heterosystem (calculated values are listed in Table 1) for *n*-CdS / *p*-CdTe (a) and *n*-ZnS / *p*-CdTe (b) HJs. It should be noted that the calculated values of Q for these HJs are close, which could be explained by a small difference in height of the potential barriers in these structures (Table 1).

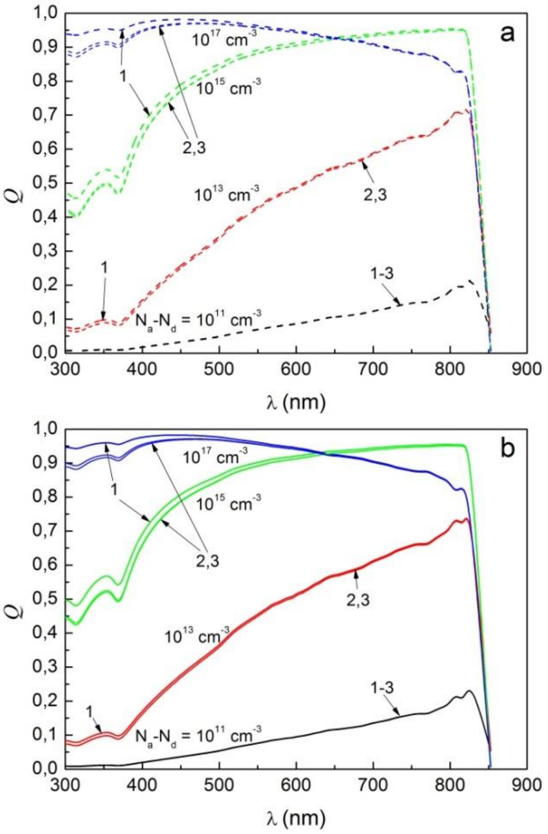

Fig. 1 – Calculated quantum yield (Q) of SC at different values of uncompensated acceptors concentration in the layer of CdTe $(N_a - N_d)$ and recombination velocity (S: 1 – 10^7 cm/s, 2 – 10^8 cm/s, 3 – 10^9 cm/s) for *n*-CdS/*p*-CdTe (a) HJ and *n*-ZnS/*p*-CdTe (b)

As shown in Fig. 1 if $(N_a - N_d) = 10^{11}$-10^{15} cm^{-3} while increasing the wavelength of the light flux an increase of the quantum yield of SC occurs, herewith this index takes the maximum values at the photon energy close to the width of CdTe ($\lambda \approx 840$ nm) band gap. Calculations show that quantum yield acquires the biggest values at a concentration of uncompensated acceptors 10^{15}-10^{17} cm^{-3}, i.e., at the width of the space charge region at absorbing material d = (0.11-1.08) μm. The last value is close to thickness of the region of 98 % CdTe light absorption. Thus, presence of the electric field in absorption area of radiation leads to a significant increase in the quantum yield of SC. The analysis shows that the doping of the absorbing material to the values ($N_a - N_d$) = 10^{15}-10^{17} cm^{-3} is optimal to maximize the efficiency of solar cells based on considered HJ.

From the graphs presented in Fig. 1 one can see that the surface recombination has a greater impact on the value of the quantum yield at a lower concentration of uncompensated acceptors (wider space charge region). It should be noted that the increase of recombination velocity at the HJ interface (10^8-10^9) cm/s expectedly results in the reduction of the quantum yield of solar cells. This dependence is more vivid at values ($N_a - N_d$) = (10^{15}-10^{17}) cm^{-3} at a wavelength (300-500) nm (Fig. 1).

3. DETERMINATION OF SC'S DENSITY OF SHORT CIRCUIT CURRENT (J_{SC})

Short-circuit current density of SC (J_{sc}) can also be calculated by the formula [14]:

$$J_{кз} = q\sum_i T\ \lambda\ \frac{\varphi_i\ \lambda_i}{h\nu_i} Q\ \lambda_i\ \Delta\lambda_i\ , \qquad (3)$$

where, φ_i – spectral power density of solar-radiation; $\Delta\lambda_i$ – interval between successive values of wavelength λ_i

Calculation of short-circuit current was carried by radiation of SC by solar radiation in terms of AM 1.5 (table ISO 9845-1:1992). It should be noted that the loss of light by recombination was calculated for the barrier height of 0.70 eV in case of HJ *n*-CdS / *p*-CdTe [19] and 0.82 eV – HJ *n*-ZnS / *p*-CdTe [20].

Fig. 2 shows graphs of influence of recombination losses on the short circuit current density in SC ITO/CdS/CdTe and ZnO/ZnS/CdTe at different values of concentration of uncompensated acceptors and recombination velocity ($S = 10^7$-10^9 cm/s). As can be seen from the figure, for ZnO/ZnS/CdTe SC value of short circuit current density decreases slightly while increasing thickness of the window layer and the doping level of CdTe layer (the width of the space charge region). However, for ITO/CdS/CdTe SC inverse relationship is observed. In all presented in Fig. cases, the increase of recombination velocity leads to a decrease of J_{sc} values, herewith the largest effect is observed when the thickness of the window layer is 50 nm.

The biggest difference of these values of J_{sc} between given SC structures in these conditions appears at 50 nm window layer thickness and is equal to (2.5-6) mA/cm^2.

Analyzing Fig. 2, it should be noted that with increase of the concentration of uncompensated acceptors to 10^{17} cm^{-3} in the CdTe absorber layer and different values of the thickness of the window layers short-circuit current J_{sc} for multilayer structures ITO/CdS/CdTe and ZnO/ZnS/CdTe SC takes the following values: 16.67 mA/cm^2, 18.82 mA/cm^2 ($d_{\text{ITO(ZnS)}}$ = 50 nm); 18.35 mA/cm^2, 18.44 mA/cm^2 ($d_{\text{ITO(ZnS)}}$ = 300 nm), accordingly.

Note that from a physical point of view open circuit voltage (U_{oc}) cannot exceed the height of the potential barrier of HJ.

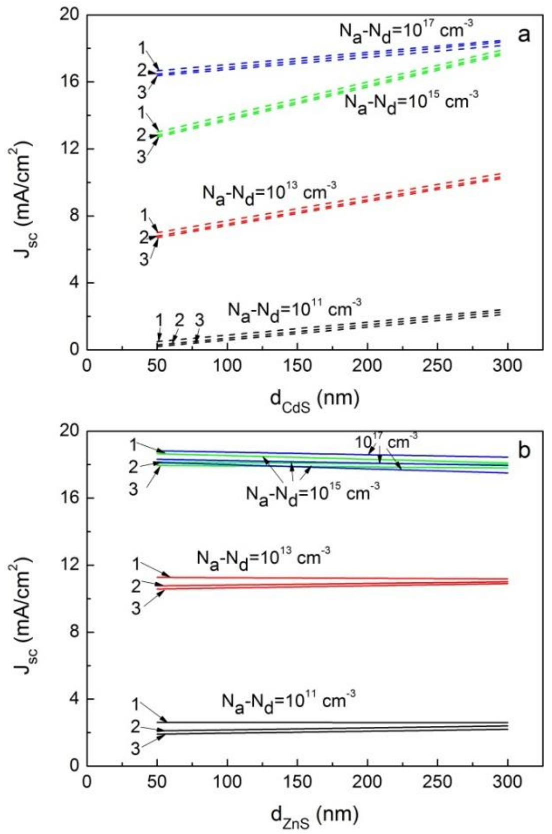

Fig. 2 – Short-circuit current density (J_{sc}) for SC of ITO/CdS/CdTe (a) and ZnO/ZnS/CdTe (b) type depending on the thickness of the window layer, the concentration of uncompensated acceptors ($N_a - N_d$) and recombination velocity (S: 1 – 10^7 cm/s, 2 – 10^8 cm/s, 3 – 10^9 cm/s)

4. INFLUENCE OF RECOMBINATION LOSSES ON SC EFFICIENCY

The effectiveness of the SC η (%) can be calculated by the formula [9]

$$\eta = \frac{U_{xx} \cdot J_{кз} \cdot FF}{P_{вх}} \qquad (4)$$

where U_{oc} – open circuit voltage of SC; J_{sc} – short-circuit current density; FF – fill factor; P_{in} – input power

Table 2 indicates the parameters of real photovoltaic devices that were used for further calculations.

Table 2 – Values of the main parameters of the actual ITO/CdS/CdTe and ZnO/ZnS/CdTe SC to determine the efficiency of photoconversion

SC structure	U_{oc}, mV	FF, %	P_{in}, mV/cm^2	Reference
ITO/CdS/CdTe	0.572	63	100	[1]
ZnO/ZnS/CdTe	0.817	80		[5]

Fig. 3 shows the dependence of the efficiency of the SC on the thickness of the window layer (CdS, ZnS) and doping level of the absorbing layer.

From Fig. 3 one can see that SC with the structure of ZnO/ZnS/CdTe at a concentration of uncompensated acceptors (10^{15}-10^{17} cm^{-3}) and recombination velocity

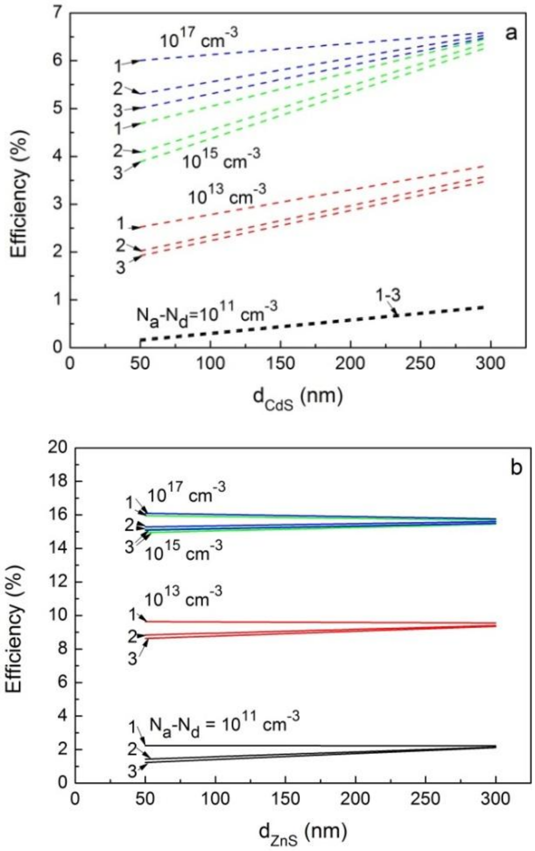

Fig. 3 – Effect of recombination losses on efficiency of SC with the structure of ITO/CdS/CdTe (a) and ZnO/ZnS/CdTe (b) depending on the thickness of the window layer, the concentration of uncompensated acceptors ($N_a - N_d$) and recombination velocity (S: 1 – 10^7 cm/s, 2 – 10^8 cm/s, 3 – 10^9 cm/s)

($S = 10^7$ cm/s) have the largest values of efficiency (15.9-16.1 %). These values are close to the obtained values for the actual ITO/CdS/CdTe SC, that indicates about their good optimization.

For solar cells with the structure of ZnO/ZnS/CdTe with decreasing the concentration of uncompensated acceptors ($N_a - N_d$) to 10^{11} cm^{-3} and increasing S the conversion efficiency of photoconverters dramatically reduces to ≈ 3 %. It was established that the value of SC with the structure of ITO/CdS/CdTe are lower of (2-14 %) depending on the thickness of the window layer, width d, S velocity than ZnO/ZnS/CdTe.

CONCLUSIONS

In this paper the recombination losses in SC-based on n-ZnS/p-CdTe and n-CdS / p-CdTe HJ with frontal conductive contact ITO and ZnO were identified and compared.

It was found that the calculated value of the quantum yield of SC takes the maximum values at photons energy close to E_g CdTe ($\lambda \approx 840$ nm), concentration of uncompensated acceptors 10^{15}-10^{17} cm^{-3} and the recombination velocity 10^7 cm/s. As the length of the incident radiation decreases the value of Q, associated with surface recombination of light generated charge carriers, decreases. Surface recombination to a greater degree influences the values of the quantum yield at lower concentration of uncompensated acceptors.

It was found that SC with the structure of ZnO/ZnS/CdTe at a concentration of uncompensated acceptors (10^{15}-10^{17} cm^{-3}), $d = 50$ nm and $S = 10^7$ cm/s have the biggest values of efficiency (15.9-16.1 %). The value of efficiency for SC with the structure ITO/CdS/CdTe are lower of (2-14 %) depending on the thickness of the window layer d, S velocity and concentration ($N_a - N_d$).

The carried calculations make it possible to determine the maximum value of the real efficiency of solar cells with consideration of recombination losses in the layers of solar cells and optimize their design.

REFERENCES

1. S. Girish Kumar, K.S.R. Koteswara Rao, *Energ. Environ. Sci.* **7**, 45 (2014).
2. S.M. Sze, *Physics of Semiconductor Devices (2nd Edition)* (Amsterdam: Wiley: 1981).
3. H. Kim, K. Cha, V.M. Fthenakis, P. Sinha, T. Hur, *Sol. Energy* **103**, 78 (2014).
4. L. Kranz, S. Buecheler, A.N. Tiwari, *Sol. Energ. Mat. Sol. C* **119**, 278 (2013).
5. M.A. Green, K. Emery, Y. Hishikawa, W. Warta, *Progr. Photovolt.: Res. Appl.* **21**, 827 (2013).
6. J. Poortmans, V. Arkhipov, *Thin Film Solar Cells: Fabrication, Characterization and Application* (Chichester: John Wiley&Sons: 2006).
7. L.A. Kosjachenko, E.V. Grushko, *Ukr. Fiz. Zhurn. Ogljadi* **7**, 3 (2012).
8. A. Rios-Flores, O. Ares, J.M. Camacho, V. Rejon, J.L. Pena, *Sol. Energy* **86**, 780 (2012).
9. R. Scheer, H. Werner Schock, *Chalcogenide Photovoltaics. Physics, Technologies and Thin Film Devices* (Weinheim: Wiley-VCH, 2011).
10. M.M. Ivashchenko, D.I. Kurbatov, A.S. Opanasyuk, I.Yu. Protsenko, H. Cheong, *J. Nano Electron. Phys.* **4** No 1 01024-1 (2012).
11. D.H. Shin, J.H. Kim, Y.M. Shin, K.H. Yoon, E.A. Al-Ammar, B.T. Ahn, *Progr. Photovolt: Res. Appl.* **21**, 217 (2013).
12. G. Contreras-Puente., O. Vigil, M. Ortega-Lopez, *Thin Solid Films* **378**, 361 (2000).
13. U. Gangopadhyay, K. Kim, D. Mangalaraj, Junsin Yi, *Appl. Surf. Sci.* **230**, 364 (2004).
14. H.A. Mohamed, *J. Appl. Phys.* **113**, 093105 (2013).
15. L.A. Kosyachenko, E.V. Grushko, V.V. Motushchuk, *Sol. Energ. Mat. Sol. C* **90**, 2201 (2006).
16. O.A. Dobrozhan, T.O. Berestok, D.I. Kurbatov, A.S. Opanasyuk, N.M. Opanasyuk, V.F. Nefedchenko, *Proc. NAP-2013, art. no. 04NEA16* (Alushta: 2013).
17. L.A. Kosyachenko, V.M. Sklyarchuk, Ye.F. Sklyarchuk, K.S. Ulyanitsky, *Semicond. Sci. Technol.* **14**, 373 (1999).
18. S. Adachi, *Handbook of Physical Properties of Semiconductors* (Boston: Kluwer Academic Publishers: 2004).
19. G.S. Khripunov, *Semiconductors* **40**, 113 (2006).
20. D.I. Kurbatov, V.V. Kosyak, M.M. Kolesnyk, A.S. Opanasyuk, S.N. Danilchenko, Yu.P. Gnatenko, *Mater Chem. Phys.* **138**, 731 (2013).