THE EFFECT OF OPTICAL AND RECOMBINATION LOSSES IN CU₂ZNSN(S,SE)₄-BASED THIN-FILM SOLAR CELLS WITH CDS, ZNSE, ZNS WINDOW AND ITO, ZNO CHARGE-COLLECTING LAYERS

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Abstract: *We reported the investigation the effect of the optical and recombination losses in solar cells (SCs) based on n-CdS(ZnSe, ZnS)/p-Cu₂ZnSn(S,Se)₄ heterojunctions with n-ITO(ZnO) frontal charge-collecting contacts on the internal (Q_{int}), external (Q_{ext}) quantum yields, short-circuit current density (J_{sc}) and maximum efficiency (η) of solar cells*

KEYWORDS: CU₂ZNSNS₄ FILMS; OPTICAL LOSSES; RECOMBINATION LOSSES; QUANTUM YIELD; SHORT-CIRCUIT CURRENT; EFFICIENCY.

1. Introduction

The future forecast for the renewable energy demonstrates that the solar power will become the dominant energy source from the middle of the 21st century. One of the most perspective routes to utilize the solar energy is its conversion into electricity by using the solar cells (SCs).

Nowadays, the silicon-based SCs are the most commercialized and widespread technology. But alternative are thin-film SCs based on CdS/*p*-CdTe heterojunction (HJ) with *n*-ITO frontal charge-collecting contact have also been widely spread on the photovoltaic market [1, 2]. However, the shortcomings, such as toxicity of Cd, high price and low abundance of In and Te, give rise to the search for the alternative materials to the functional layers in the photovoltaic devices. Nowadays, the compound Cu₂ZnSn(S,Se)₄ (CZTSSe) is regarded as a promising substitute for the traditional Si, CdTe, Cu(In,Ga)(S,Se)₂ absorber layers. CZTSSe possesses the controlled band gap for the solar light absorption (E_g^{CZTSSe} = 1.0-1.5 eV), *p*-type conductivity and high absorption coefficients ($\alpha \sim 10^4$-10^5 cm^{-1}) [3, 4]. The promising alternatives for the well-known SCs are considered the structure with ZnSe or ZnS window layers and ZnO charge collecting contact [5-7]. These structures contain only the abundant and non-toxic elements. ZnS, ZnO, ZnSe (E_g^{ZnS} = 3.68 eV, E_g^{ZnO} = 3.37 eV, E_g^{ZnSe} = 2.67 eV) are the wide-band gap semiconductors allowing to increase the number of the photons incoming to CZTSSe absorber layer.

According to Shockley-Queisser analysis, the maximum theoretical efficiency of the thin-film SCs with CZTSSe absorber layer is about (32-34) % [3, 8]. However, the experimental efficiency of CZTSSe SCs is only 12.6 % [9, 10]. The difference between the theoretical and experimental values of the efficiency can be explained by the optical, electrical and recombination losses which take place during the conversion of the solar energy into electricity.

The enhancement of the SC efficiency might be achieved by the minimization of the described losses by using the optimized structures based on the functional layers with the improved characteristics.

The foregoing discussions identified the main goal of this work – to determine and compare the optical and recombination losses in the SCs based on *n*-CdS(ZnSe, ZnS)/*p*-CZTSSe HJs with *n*-ITO(ZnO) frontal charge-collecting contacts.

2. Methodologies

The light flow, before reaching CZTSSe absorber layer in which the generation of the electron-hole pairs is occurred, passes through the ITO(ZnO) and CdS(ZnSe, ZnS) layers of the SCs. Herewith, the optical losses of energy as a consequence of the light reflection from the air/ITO(ZnO), ITO(ZnO)/CdS(ZnSe, ZnS), CdS(ZnSe, ZnS)/CZTSSe interfaces and the light absorption of ITO(ZnO), CdS(ZnSe, ZnS) are observed.

The reflection coefficients at the interfaces of the contacted layers can be determined by using Fresnel equation [11]:

$$R = \left(\frac{n_i - n_j}{n_i + n_j} \right)^2 \tag{1}$$

where n_i, n_j – refractive indices of the first and second contacted materials, respectively.

In the case of the electrically conductive material, the reflection coefficients might be calculated by using the following expression [12]:

$$R_{ij} = \left| \frac{n_i^* - n_j^*}{n_i^* + n_j^*} \right| = \frac{(n_i - n_j)^2 + (k_i - k_j)^2}{(n_i + n_j)^2 + (k_i + k_j)^2} \tag{2}$$

where n_i^*, n_j^* – the complex refractive indices; k_i, k_j – the extinction coefficients.

The spectral dependencies of *n* and *k* were taken from the literature data on the refractive and extinction coefficients of ITO, ZnO, CdS, ZnSe, ZnS, CZTS [3, 13, 14]. It was assumed that the air has *n* = 1 and *k* = 0.

The transmission coefficients taking into account both the light reflection and absorption of the charge-collecting and window layers can be calculated using the expression [11, 15]:

$$T(\lambda) = (1 - R_{12})(1 - R_{23})(1 - R_{34})(1 - R_{45}) \exp(-\alpha_1 d_1) \exp(-\alpha_2 d_2) \tag{3}$$

where α_1, α_2 – the absorption coefficients of the charge-collecting and window layers; d_1, d_2 – the charge-collecting and window layer thicknesses.

The absorption coefficients of the materials $\alpha(\lambda)$, considering the extinction coefficient $k(\lambda)$, can be calculated by using the following equation [11]:

$$\alpha(\lambda) = \frac{4\pi}{\lambda} k \tag{4}$$

The modeling of the light reflection and absorption processes in the multilayer structures was carried out by using the different thicknesses of the window, $d_{CdS(ZnSe, ZnS)}$ = (25-100) nm, and frontal charge-collecting, $d_{ITO(ZnO)}$ = (100-200) nm, layers. These thickness values of the layers are typical for the practical SCs.

The important parameter for the analysis of the recombination losses in the SCs is the width of space charge region (w), in other words, the depletion region, occurring at the interface between the heteropairs, where the electrical field is acting as a separator for the photogenerated electron-hole pairs.

This width mainly depends on the concentration of uncompensated acceptors ($N_a - N_d$) (i.e., the difference between the acceptor and donor concentrations), locating in the semiconductor materials, and the contact barrier height. However, the latter value for the investigated junctions, unfortunately, was not known. This problem was solved by means of the construction of the energy band diagrams of the HJs.

It was considered that the small amount of the surface states exists at the interface between heteropairs. At the same time, the charge transport mechanism was described accordingly to Anderson model.
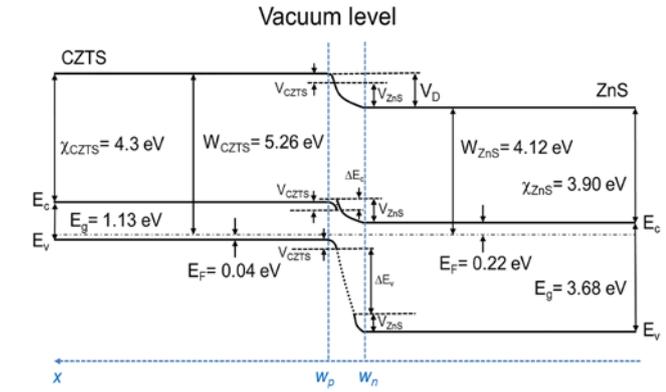

Fig. 1. Energy band diagrams of n-ZnS/p-CZTS HJ.

Unlike the fact that the charge transport processes at n-CdS/p-CdTe HJ are analogous to those occurring in the Schottky diodes [1], the same charge transport mechanisms for n-CdS(ZnSe, ZnS)/p-CZTS heterosystems are not acceptable. It is due to the fact that the doping levels in CZTS ($N_a = 10^{17}$-10^{18} cm^{-3} [16]) are higher than in CdTe material ($N_a = 10^{14}$-10^{17} cm^{-3} [17]) and even higher than in the window materials ($N_d = 10^{16}$-10^{17} cm^{-3} [14]). It means that SCR is located both in the window (w_n) and absorber (w_p) layers, and SCR width can be determined by the equations [18]:

$$w = \sqrt{\frac{2\varepsilon_n\varepsilon_p\varepsilon_0(V_D - qU)}{q^2}\left(\frac{1}{\varepsilon_n N_D} + \frac{1}{\varepsilon_p N_A}\right)} \quad (5)$$

where ε_n, ε_p – the relative permittivity of the window and absorber materials; ε_0 – the vacuum permittivity; $V_D = qV_{bi}$ – the contact barrier height (V_{bi} – the built-in potential); U – the applied external voltage; q – the elementary charge; N_A, N_D – the concentration of uncompensated acceptors and donors in absorber and window layers.

Kosyachenko et al. showed that the solution of the continuity equation is effective for the determination of the drift component of the internal quantum yield (Q_{drift}) of the SC, while taking into account the recombination at the HJ interface and in SCR, by using the following equation [11, 17]:

$$Q_{drift\,p(n)} = \frac{1 + \dfrac{S}{D_{p\,p(n\,n)}}\left(\alpha_{p(n)} + \dfrac{2\cdot(V_D - qU)}{w_{p(n)}\cdot kT}\right)^{-1}}{1 + \dfrac{S}{D_{p\,p(n\,n)}}\left(\dfrac{2\cdot(V_D - qU)}{w_{p(n)}\cdot kT}\right)^{-1}} - \frac{\exp(-\alpha_{p(n)}w_{p(n)})}{1 + \alpha_{p(n)}\cdot L_{n\,p(p\,n)}} \quad (6)$$

where S – the recombination velocity of the charge carriers at the HJ interface and in SCR; $D_{p\,p(n\,n)}$ – the diffusion coefficients of the holes (electrons) in the absorber (window) layers; $\alpha_{p(n)}$ – the light absorption coefficients of the absorber (window) layer; k – the Boltzmann constant; T – the temperature; $L_{n\,p(p\,n)}$ – the diffusion length of the electrons (holes) in the absorber (window) layer ($L_{n(p)} = (\tau_{n(p)}.D_{n(p)})^{1/2}$, where $\tau_{n(p)}$ – the lifetime of the electrons (holes), $D_{n(p)}$ – the diffusion coefficients of the electrons (holes) in the relevant layers).

It should be noted that the equation (6) does not consider the recombination in the quasineutral regions of the window and absorber materials and on the back surface of CZTS layer. To account these losses, the diffusion ($Q_{dif\,p(n)}$) component of the quantum yield can be evaluated by the following equation [17]:

$$Q_{dif\,p(n)} = (\alpha_{p(n)}L_{n\,p(p\,n)}/(\alpha_{p(n)}^2 L_{n\,p(p\,n)}^2 - 1))\exp(-\alpha_{p(n)}w_{p(n)})(\alpha_{p(n)}L_{n\,p(p\,n)} -$$
$$\frac{((S_b L_{n\,p(p\,n)}/D_{p\,p(n\,n)})(\cosh((d_{p(n)} - w_{p(n)})/L_{n\,p(p\,n)}) - \exp(-\alpha_{p(n)}(d_{p(n)} - w_{p(n)}))) + \sinh((d_{p(n)} - w_{p(n)})/L_{n\,p(p\,n)}) + \alpha_{p(n)}L_{n\,p(p\,n)}\exp(-\alpha_{p(n)}(d_{p(n)} - w_{p(n)}))))}{(S_b L_{n\,p(p\,n)}/D_{p\,p(n\,n)})\sinh((d_{p(n)} - w_{p(n)})/L_{n\,p(p\,n)}) + \cosh((d_{p(n)} - w_{p(n)})/L_{n\,p(p\,n)})} \quad (7)$$

where $d_{p(n)}$ – the thicknesses of the absorber and window layers; S_b – the recombination velocity in the quasineutral regions and on the back surface of the absorber layer.

The total internal quantum yield of the SCs is easy to determine as the sum of all quantum yields, considering the directions of the drift and diffusion currents in the space charge and quasineutral regions. The account of the optical losses owing to the reflection and absorption of the light by the auxiliary layers (ITO, CdS, ZnSe, ZnS) of the SCs gives the opportunity to determine the external quantum yield (Q_{ext}) of the device [11,17]:

$$Q_{ext} = T(\lambda)Q_{int} \quad (8)$$

The optical losses described in the previous subsections are important for the analysis of the SC efficiency. As a consequence of its consideration, we built the spectral dependencies of the external quantum yield (Q_{ext}) for the investigated SCs. The calculations were carried out using the following physical values: $N_a = 10^{18}$ cm^{-3}, $N_d = 1017$ cm-3, $d_{ITO(ZnO)} = 100$ nm, $d_{CdS(ZnSe,\ ZnS)} = 25$ nm, $d_{CZTS} = 1$ μm. The concentrations of uncompensated acceptors and donors coincide with SCR widths which are close to the device thicknesses. At the same time, the thicknesses of all functional layers were taken close to those used in the practical SCs [2].

The short-circuit current density (J_{sc}) of the SCs was determined using the well-known formula:

$$J_{sc} = q\sum_i T(\lambda)\frac{\Phi_i(\lambda_i)}{hv_i}Q_{int}(\lambda_i)\Delta\lambda_i \quad (9)$$

where $\Phi_i(\lambda_i)$ – the spectral power density of the solar radiation; $\Delta\lambda_i$ – the interval between neighboring values of the wavelength; hv_i – the photon energy.

The calculation of J_{sc} was carried out under AM 1.5G radiation conditions [19]. Herewith, the maximum short-circuit current density ($J_{max\,sc}$) can be obtained by neglecting the light losses owing to the absorption of the auxiliary layers, i.e. $T(\lambda) = 1$, and under the circumstance that every photon generates the electron-hole pair which reaches the charge-collecting contacts without recombination, i.e. $Q_{ext}(\lambda) = 1$. It was established, that the maximum value of the short-circuit current density of the investigated SCs is equaled to $J_{max\,sc} = 34.82$ mA/cm^2.

The solar cell efficiency (η) is determined by the well-known equation [10, 29, 38]:

$$\eta = \frac{U_{oc}\cdot J_{sc}\cdot FF}{P_{in}} \quad (10)$$

where U_{oc} – the open-circuit voltage; J_{sc} – the short-circuit current density; FF – the fill factor; P_{in} – the input power (100 mW/cm^2, illumination AM 1.5G).

To determine the effect of the optical and recombination losses on the maximum efficiencies of the SCs with ITO(ZnO)/CdS(ZnSe, ZnS)/CZTS structures, the values of open-circuit voltage were taken as those that coinciding with the height of

the contact potential differences at the HJs: U_{oc} = (0.72 V)$_{CdS}$, (1.07 V)$_{ZnSe}$, (1.14 V)$_{ZnS}$, and the values of the fill factor that matching the maximum possible FF = 89 % [5]. Accordingly, it was found that the maximum efficiency of the single junction SC was 33.5% [5].

3. Results and discussions

The analysis of the optical losses owing the light reflection and absorption of the window and charge-collecting layers showed that, as it was expected, the replacement of the traditional window material (CdS) with wide band gap materials (ZnSe, ZnS) caused the increase of the transmission coefficients of the multilayer structures, primarily, in the short wave region with $d_{CdS(ZnSe, ZnS)}$ = (25-100) nm. This tendency was valid for applying ITO and ZnO layers with $d_{ITO(ZnO)}$ = (100-200) nm as the charge-collecting contacts.

ZnO layer is more attractive than ITO because it improves the light transmission coefficients toward CZTS absorber layer regardless of the considered window materials.

However, it should be noted that the values of T for the best and worst structures differed only in (5.2-13.5) %.
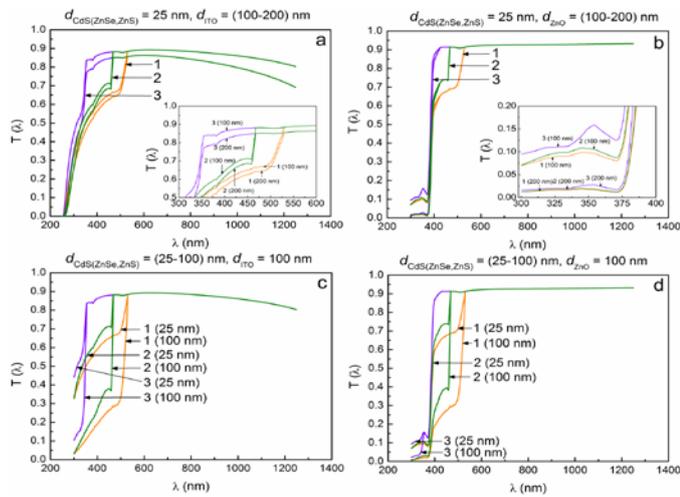

Fig.2. *Spectral dependencies of the transmission coefficients of the SCs with the structures ITO/CdS/CZTS (1), ITO/ZnSe/CZTS (2), ITO/ZnS/CZTS (3) (a, c); ZnO/CdS/CZTS (1), ZnO/ZnSe/CZTS (2), ZnO/ZnS/CZTS (3) (b, d) with the different thicknesses of the window and charge-collecting layers. The light reflection from the interfaces and absorption of the auxiliary layers were taken into account.*

It was established that the increase of the donor concentration in the window material at the constant values of N_a in the absorber layer resulted in the increase of the quantum efficiency of the SC based on n-CdS/p-CZTS HJ in the photosensitive region for both CZTS and CdS materials. However, this increase had a weak influence on the internal quantum yield in the photosensitive region of the window materials in the SCs based on n-(ZnSe, ZnS)/p-CZTS HJs. For the investigated HJs, the increase of the donor concentration caused the increase of the quantum yields in both middle and long wavelength regions, due to the extension of SCR in the absorber layer, and, as a consequence, reduced impact of the diffusion component on the total photocurrent (J_{ph}).

The analysis of the obtained dependencies showed that the values of Q_{ext} of the SC based on n-ZnS/p-CZTS HJ were slightly higher than those of the structure with CdS and ZnSe window layers regardless of the material of the charge-collecting contacts. Thus, as it was expected, SCs with the window layers, which possess the higher values of the band gap, demonstrated the higher quantum yields.
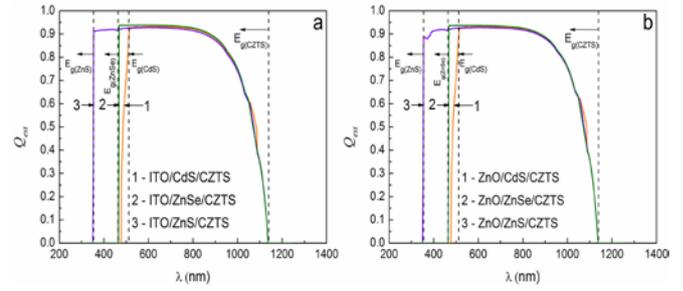

Fig. 3. *Spectral dependencies of the external quantum yield (Q_{ext}) of the SCs based on n-CdS(ZnSe, ZnS)/p-CZTS HJs with ITO (a) and ZnO (b) charge-collecting layers with: $N_a = 10^{18}$ cm^{-3}, $N_d = 10^{17}$ cm^{-3}, $d_{ITO (ZnO)} = 100$ nm, $d_{CdS (ZnSe,ZnS)} = 25$ nm, $d_{CZTS} = 1$ μm.*

However, it should be noted that we neglected the inequality state at the interfaces of the different HJs. However, in reality, the mismatch density of the dislocations at the interfaces of the considered HJs is varied.

The dependencies of the SC efficiencies (η) on the thicknesses of the window (CdS, ZnSe, ZnS) and charge-collecting (ITO, ZnO) layers are presented in Fig. 3. As can be seen from Fig. 4, the best devices,
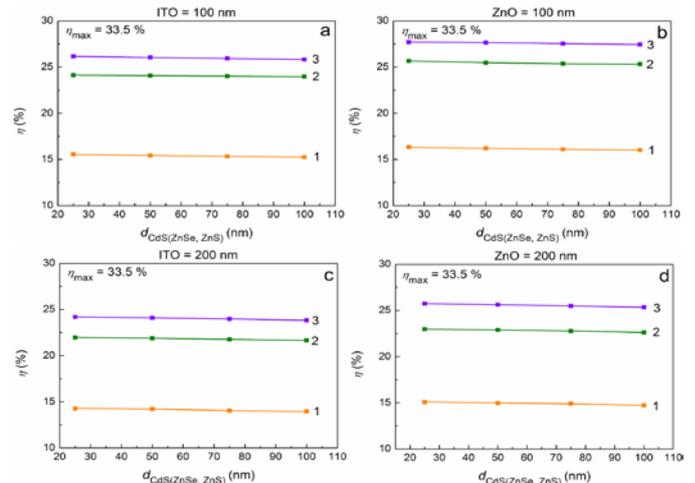

Fig.4. *The effect of the optical and recombination losses on the efficiency of the SCs based on CdS/CZTS (1), ZnSe/CZTS (2), ZnS/CZTS (3) HJs with the variable thicknesses of the window layers and two constant thicknesses of the charge-collecting contacts: 100 nm (a, b) and 200 nm (c, d).*

among the investigated SC structures, contain ZnS window layer (η = 23.8-27.7 %), and the highest values of the efficiency were demonstrated by a device with ZnO/ZnS/CZTS structure (η ~ 28 % with $d_{ZnO} = 100$ nm, $d_{ZnS} = 25$ nm).

It should be mentioned, that the efficiency of the well-known SC with ITO/CdS/CZTS structure was about (13.9-15.5) %. These values are well correlated with the results obtained for the best SC with the analogous structure (η = 12.6 %) [9]. The SCs with ZnSe window layer showed the quite high efficiencies as well, η = (21.7-25.7) %.

4. Conclusions

It was found that, under the consideration of the losses owing to the reflection and absorption of the auxiliary layers of devices, the values of J_{sc} of the SCs with the ZnO/ZnS/CZTS (d_{ZnS} = (25-100) nm, $d_{ITO(ZnO)}$ = 100 nm) structure were higher in (3.06-3.27) mA/cm^2 than those obtained for devices with ITO/CdS/CZTS structure in the overall interval of the thickness alteration. The increase of the charge-collecting layer thickness up to 200 nm led to the decrease of J_{sc} and the difference between the best (ZnO/ZnS/CZTS) and worst (ITO/ZnSe/CZTS) structures of the SCs was found to be ~3.15 mA/cm^2. It should be noted that the

optical and recombination losses caused the decrease of J_{sc} by (21.5-37.4) %.

The best devices, among the investigated SC structures, contain ZnS window layer (η = 23.8-27.7 %), and the highest values of the efficiency were demonstrated by the device with ZnO/ZnS/CZTS structure ($\eta \sim$ 28 % with d_{ZnO} = 100 nm, d_{ZnS} = 25 nm). The SCs with ZnSe window layer showed the quite high efficiency as well, η = (21.7-25.7) %. It should be mentioned, that the efficiency of the well-known SC with ITO/CdS/CZTS structure was about (13.9-15.5) %. These values are well correlated with the results obtained for the best SC with the analogous structure (η = 12.6 %).

The presented results show the maximum values of the efficiencies of the SCs based on n-CdS(ZnSe, ZnSe)/p-CZTS HJs and open the way for the optimization of the practical thin film SCs.

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