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Photoelectrical analysis of n-TiO_2/p-CdTe heterojunction solar cells

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Abstract. Photoelectrical properties of n-TiO_2/p-CdTe heterojunction solar cells were investigated under different light conditions, taking into account the presence of series and shunt resistances. The effect of light dependent dominating charge transport mechanism based on tunnel-recombination processes at the TiO_2/CdTe heterojunction interface was taken into consideration. The width W of the space charge region of the $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ solar cells and consequently the concentration of uncompensated acceptors $N_A - N_D$ were determined using the open-circuit method.

Keywords: TiO_2, CdTe, heterojunction, solar cell.

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1. Introduction

CdTe-based heterojunction solar cells are very prospective due to their optimal photoelectrical characteristics for highly efficient solar energy conversion. It is known that CdS/CdTe solar cells are the most studied among promising CdTe-based solar cells [1–7]. However, wide band gap conductive metal oxides/CdTe heterojunctions become very attractive due to the wide spectral range of their photosensitivity. In particular, a number of research gropes have shown that anisotype heterojunctions $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ are prospective for application in photovoltaics, in spite of some drawbacks resulted from non-optimal conduction bands alignment and recombination at the TiO_2/CdTe heterojunction interface [8–12].

In our previous works [12, 13] the detailed investigation of electrical properties of $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ heterojunctions was carried out under dark and different light conditions. The dominating current transport mechanisms through the heterojunctions were established under dark conditions as well as their light dependence was shown. However, there was not paid enough attention to the analysis of their photoelectrical properties, which are very important for photovoltaic devices.

This paper reports the results of a detail investigation of the photoelectrical properties of $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ heterojunction solar cells in the scope of the generally accepted equivalent circuit in the presence of series and shunt resistance. The effect of the dominating light dependent tunnel-recombination current transport mechanism at forward biases will be taken into consideration. The width of the space charge region W and thus the concentration of uncompensated acceptors $N_A - N_D$ will be determined using the technique based on the open-circuit analysis of heterojunction solar cells under monochromatic illumination [14].

2. Experimental methods

The fabrication of n-TiO_2/p-CdTe heterojunction solar cells was carried out by means of the pure TiO_2 thin films deposition (σ = $0.77\,\Omega^{-1}\mathrm{cm}^{-1}$ and n = $4.8\cdot10^{17}\,\mathrm{cm}^{-3}$ at 295 K) onto freshly cleaved CdTe single crystal substrates with dimensions 5×4×1 mm

($\sigma = 8.9\cdot10^{-2}\,\Omega^{-1}\mathrm{cm}^{-1}$ and $p = 7.2\cdot10^{15}\,\mathrm{cm}^{-3}$ at 295 K) by means of the DC reactive magnetron sputtering. Simultaneously, the TiO_2 thin film was deposited onto a quartz substrate in order to measure its transmittance and electric properties.

The frontal electric contact to the solar cells was prepared by thermal evaporation of indium. The back electric contact was fabricated by successive deposition of gold and cupper layers onto the previously laser treated back surface of CdTe substrate.

More detailed description of the technological conditions of the $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ heterojunction solar cells fabrication can be found in our previous work [12].

The sources of monochromatic light (λ = 650 nm, $I_{opt} = 6\ \mathrm{mW\cdot cm^{-2}}$) and white light ($I_{opt} = 100\ \mathrm{mW\cdot cm^{-2}}$), used in our study, were a semiconductor laser and halogen lamp, respectively. A water filter was used in order to prevent the heating of the heterojunctions under white light illumination.

The transmission spectrum of the TiO_2 thin film was measured by means of a conventional spectrophotometer (SF-2000). The $I-V$ characteristics of the $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ solar cells were measured using a SOLARTRON SI 1286, SI 1255 complex.

3. Results and discussion

As was mentioned above, the analysis of the $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ solar cells will be carried out in the scope of the equivalent circuit which takes into consideration the presence of series R_s and shunt R_{sh} resistance (Fig. 1). The external current I is given as: $I = I_{ph} - I_d - I_{sh}$, where I_{ph} is the photocurrent, I_d is the diode current and I_{sh} is the current through the shunt resistance R_{sh}.

The dark $I-V$ characteristics of the $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ heterojunction solar cells measured at different temperatures were analyzed in order to determine the expression for the diode current I_d [12]. Fig. 2 shows the forward branches of the dark $I-V$ characteristics of the solar cells in the semilogarithmic scale. It is seen linear segments that provides evidence of an exponential dependence within the range of forward biases $3kT/e < V < 0.7$ V (it is the entire range of the forward biases of our interest in this study, since the maximum value of the open-circuit voltage V_{oc} = 0.69 V). The slope of the linear segments $\Delta\ln(I)/\Delta V$ does not depend on temperature. Therefore, the dominating current transport mechanism through the $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ heterojunctions was established to be the tunnel-recombination processes via defects states located in the vicinity of the heterojunction interface. In this case the diode current I_d is governed by the following equation, which takes into account the effect of series resistance R_s [15]:

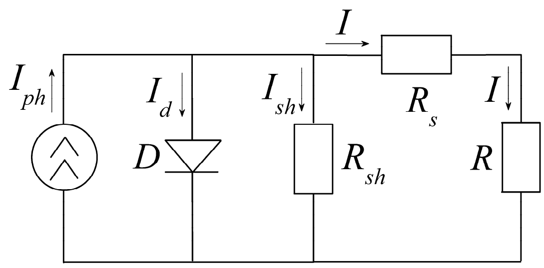

Fig. 1. The equivalent circuit of n-TiO_2/p-CdTe solar cells.

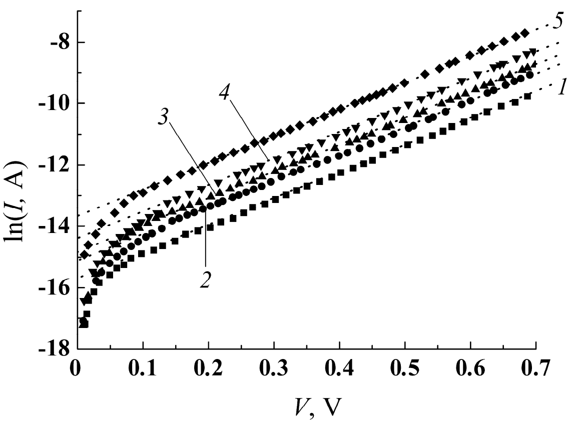

Fig. 2. The dark *I–V* characteristics of the n-TiO_2/p-CdTe heterojunction solar cells in the semilogarithmic scale: 1 – 295 K, 2 – 309 K, 3 – 318 K, 4 – 329 K, 5 – 350 K.

$$I_d = B\exp\{-\alpha_0[\varphi_0 - q(V + IR_s)]\}, \qquad (1)$$

where the coefficient $\alpha_0 = 9.5\,\mathrm{eV^{-1}}$ is determined from the slope of the linear segments the coefficient $B = 9\cdot10^{-5}\,\mathrm{A}$ is determined by means of the extrapolation of the linear segment at 295 K toward the interception with the current axis, φ_0 = 0.69 eV is the height of the potential barrier at 295 K.

Thus, we can write the expression for the light $I-V$ characteristic of the $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ heterojunction solar cell as follows:

$$I = I_{ph} - B\exp\left(-\alpha_0[\varphi_0 - q(V + IR_s)]\right) - \frac{V + IR_s}{R_{sh}}. \qquad (2)$$

The measured $I-V$ characteristic of the $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ heterojunction solar cell under white light illumination ($I_{opt} = 100\ \mathrm{mW\cdot cm^{-2}}$) is shown in Fig. 3. The values of the series R_s and shunt R_{sh} under light conditions can be easily determined using the following relations [16]:

$$R_s = \left|\frac{dV}{dI}\right|_{I=0}, \quad R_{sh} = \left|\frac{dV}{dI}\right|_{V=0}. \qquad (3)$$

Now let us write equation (2) in the case of short-circuit and open-circuit conditions, expressions (4) and (5), respectively:

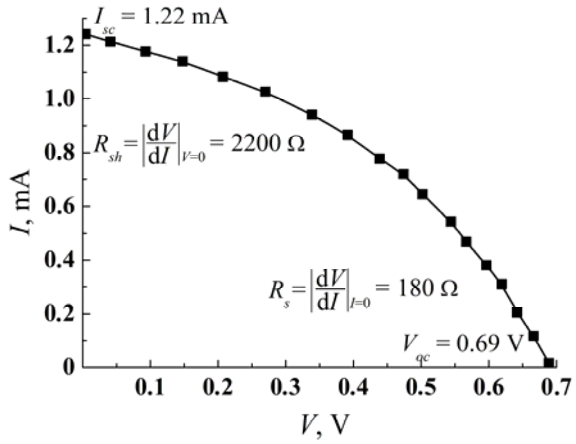

Fig. 3. The *I–V* characteristic of the n-TiO$_2$/p-CdTe solar cells under white light illumination (I_{opt} = $100\ \mathrm{mW\cdot cm^{-2}}$).

$$I_{sc}=I_{ph}-B\exp\left(-\alpha_0\left[\varphi_0-q\left(V+I_{sc}R_s\right)\right]\right)-\frac{I_{sc}R_s}{R_{sh}}, \quad (4)$$

$$I_{ph}=B\exp\left(-\alpha_0\left[\varphi_0-qV_{oc}\right]\right)+\frac{V_{oc}}{R_{sh}}.Q \quad (5)$$

On the basis of Eqs. (4) and (5) one can easy derive the following transcendental equation:

$$TE(V_{oc})=\frac{1}{B}\left(I_{sc}+B\exp\left(-\alpha_0\left(\varphi_0-qI_{sc}R_s\right)\right)+\frac{I_{sc}R_s}{R_{sh}}-\frac{V_{oc}}{R_{sh}}\right)-$$
$$-\exp\left(-\alpha_0\left(\varphi_0-qV_{oc}\right)\right)=0. \quad (6)$$

Eq. (6) is a dimensionless transcendental equation, which is considered in our case as a function of open-circuit voltage V_{oc} if all other parameters are known. The first step will be the calculation of the open-circuit voltage V_{oc} using the previously determined values of coefficients α_0 = $9.5\,\mathrm{eV^{-1}}$ and B = $9\cdot10^{-5}\,\mathrm{A}$ under dark conditions [12] and that of the short-circuit current I_{sc} = $1.22\cdot10^{-3}\,\mathrm{A}$, the series R_s = 180 Ω and shunt R_{sh} = 2.2·10^3 Ω resistance determined from the light $I-V$ characteristic shown in Fig. 3.

The value of the open-circuit voltage V_{oc} = 0.93 V, calculated by means of equation (6) using the above given values of the parameters (Fig. 4, curve 1) does not correlate with the experimentally measured value V_{oc} = 0.69 V (Fig. 3).

It is quite obvious that the values of some parameters are given wrong. The values of I_{sc}, R_s and R_{sh} are undoubtedly valid since they were determined under light conditions (Fig. 3). Therefore, we should pay more attention on coefficients α_0 and B.

It is known that the coefficients, which quantitatively describe dominating current transport mechanisms through heterojunction solar cells depend on light conditions (wavelength and intensity) [17, 18]. In our case, coefficients α_0 and B, which quantitatively describe tunnel-recombination mechanism of charge transport through n-TiO$_2$/p-CdTe solar cells also depend on light conditions [19]. Therefore the actual values of coefficients α_0 and B should also be determined under light conditions using light $I-V$ characteristics of the solar cells under investigation.

If the inequality $\exp\left[-\alpha_0\left(\varphi_0-q\left(V+IR_s\right)\right)\right]$ >> $\exp\left[-\alpha_0\left(\varphi_0-qIR_s\right)\right]$ is valid, the following equation can be written [13, 19]:

$$\ln\left[\frac{\left\{\left[I_{sc}-I\right]\left[R_s+R_{sh}\right]-V\right\}}{R_{sh}}\right]=$$
$$=\ln[B]-\varphi_0\alpha_0+q\alpha_0\left[V+IR_s\right]. \quad (7)$$

One can easily determine the actual value of the coefficient α from the slope of the linear dependence (7) in the semilogarithmic scale $\ln\left[\left\{\left(I_{sc}-I\right)\left(R_s+R_{sh}\right)-V\right\}/R_{sh}\right]$ vs. $\left(V+IR_{sh}\right)$:

$$\alpha_0=\frac{\Delta\ln\left[\frac{\left\{\left[I_{sc}-I\right]\left[R_s+R_{sh}\right]-V\right\}}{R_{sh}}\right]}{q\Delta\left[V+IR_s\right]}. \quad (8)$$

The coefficient B can be determined by the extrapolation of the linear dependence toward the interception with the current axis:

$$B=\exp\left[\varphi_0\alpha_0+\ln\left[\frac{\left\{\left[I_{sc}-I\right]\left[R_s+R_{sh}\right]-V\right\}}{R_{sh}}\right]_{\left[V+IR_s\right]=0}\right]. \quad (9)$$

Fig. 5 shows the light *I–V* characteristic of the n-TiO$_2$/p-CdTe solar cells under white light illumination (I_{opt} = $100\ \mathrm{mW\cdot cm^{-2}}$) plotted in the mentioned semilogarithmic coordinates $\ln\left[\left\{\left(I_{sc}-I\right)\left(R_s+R_{sh}\right)-V\right\}/R_{sh}\right]$ vs. $\left(V+IR_{sh}\right)$. The actual values of coefficients α_0 = $10.9\,\mathrm{eV^{-1}}$ and B = $1.05\cdot10^{-3}\,\mathrm{A}$ under given light conditions were determined from Fig. 5 using equations (8) and (9), respectively.

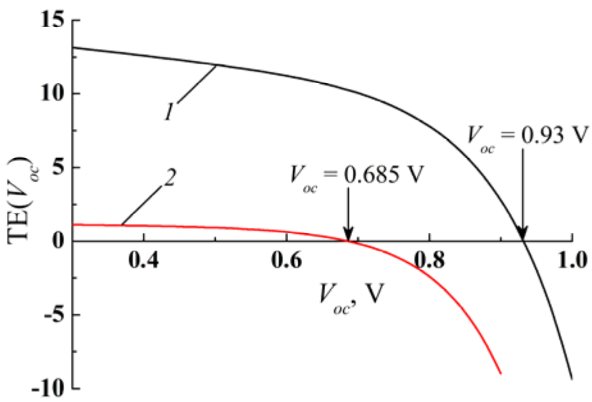

Fig. 4. The calculation of the open-circuit voltage V_{oc} under different conditions: 1) the coefficients α_0 and B are considered under dark conditions, 2) the coefficients α_0 and B are considered under light conditions.

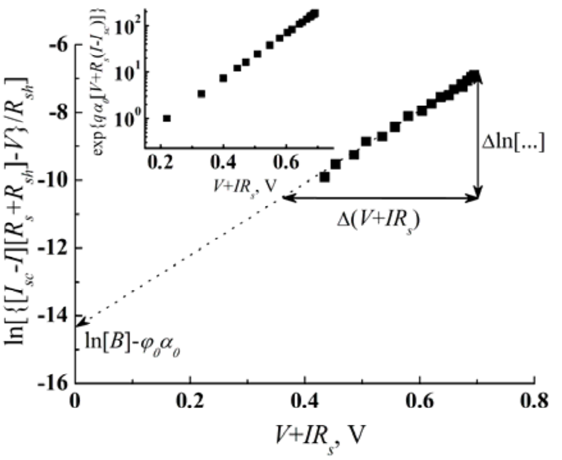

Fig. 5. The *I–V* characteristic of the n-TiO_2/p-CdTe solar cells under white light illumination (I_{opt} = 100 mW·cm^{-2}) plotted in the semilogarithmic coordinates ln[{(I_{sc} – I)(R_s + R_{sh}) – – V}/R_{sh}] vs. ($V + IR_{sh}$). The ratio exp[–α_0(φ_0 – q($V + IR_s$))] / exp[–α_0(φ_0 – qIR_s)] is shown in the inset.

Now let us apply the new values of coefficients α_0 and B instead of their previous values determined under dark conditions in equation (6) and calculate the open-circuit voltage V_{oc} again (Fig. 4, curve 2). This time the calculated open-circuit voltage under the white light illumination V_{oc} = 0.685 V is in a perfect agreement with its experimentally measured value (Fig. 3) as opposite to the result of the previous calculation (Fig. 4, curve 1).

The obtained results provide evidence of a significant effect of the light dependent tunnel-recombination mechanism of charge transport through the anisotype heterojunctions $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ under forward biases on their photoelectric parameters, in particular, open-circuit voltage V_{oc}.

In order to prove this approach under different light conditions let us apply it to the $I-V$ characteristic of the $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ heterojunction solar cells illuminated by monochromatic light (λ = 650 nm, I_{opt} = $6\ \mathrm{mW \cdot cm^{-2}}$), which is shown in Fig. 6. The series R_s and shunt R_{sh} resistance were determined from the $I-V$ characteristic (Fig. 6) using expressions (3) and are equal to 670 Ω and 25.7 kΩ, respectively.

The *I–V* characteristic was rebuild in the semilogarithmic coordinates $\ln\left[\left\{(I_{sc}-I)(R_s+R_{sh})-V\right\}/R_{sh}\right]$ vs. $(V+IR_{sh})$ (Fig. 7) in order to determine the actual values of coefficients $\alpha_0 = 15.2\,\mathrm{eV}^{-2}$ and $B = 2.4\cdot10^{-4}\,\mathrm{A}$ under the monochromatic illumination.

It should be noting that the calculated value of the open-circuit voltage V_{oc} = 0.64 (the inset (b) of Fig. 7) is equal to its experimental value under the monochromatic illumination (Fig. 6). This fact proves that the considered electrical parameters R_s, R_{sh}, α_0 and B are valid. Therefore, they can be applied for further photoelectric analysis of $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ under the monochromatic illumination.

One of the main electrical properties of the absorber layer in CdTe-based solar cells is the concentration of the uncompensated acceptors $N_A - N_D$, since it determines the width W of space charge region. The width W of depletion region effects on dominating charge transport mechanisms and quantum efficiency of solar cells, especially, under short wavelength illumination [5, 20].

It is possible to calculate W and consequently $N_A - N_D$ of the $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ heterojunction solar cells by employing the open-circuit technique, which is based on the following dimensionless transcendental equation as a function of W [14]:

$$\mathrm{TE}(W) = FT_{\mathrm{TiO_2}} \times \left[\frac{1+\dfrac{S}{D_p}\left(\alpha+\dfrac{2}{W}\dfrac{\varphi_0-qV_{oc}}{kT}\right)^{-1}}{1+\dfrac{S}{D_p}\left(\dfrac{2}{W}\dfrac{\varphi_0-qV_{oc}}{kT}\right)^{-1}} - \exp(-\alpha W) + \frac{\alpha L_n}{\alpha^2 L_n^2-1}\exp(-\alpha W)\left\{\alpha L_n - \frac{\dfrac{S_b L_n}{D_n}\left[\cosh\left(\dfrac{d-W}{L_n}\right)-\exp[-\alpha(d-W)]\right]+\sinh\left(\dfrac{d-W}{L_n}\right)-\alpha L_n\exp[-\alpha(d-W)]}{\dfrac{S_b L_n}{D_n}\sinh\left(\dfrac{d-W}{L_n}\right)+\cosh\left(\dfrac{d-W}{L_n}\right)}\right\}\right] - \frac{h\nu\left(B\exp[-\alpha_0(\varphi_o-qV_{oc})]+\dfrac{V_{oc}}{R_{sh}}\right)}{qP_{opt}} = 0 \quad (10)$$

where $F = A_i/A_{sc}$ is the shade factor of the frontal contact, A_i and A_{sc} are the illuminated and total area of the solar cell, respectively, T_{TiO2} is the transmittance of the TiO_2 thin film at λ = 650 nm, S and S_b are the recombination velocity at the heterojunction interface and back contact, D_n and D_p are the diffusion coefficient of electrons and holes, L_n is the electron diffusion length, d is the thickness of the CdTe layer, α is the absorption coefficient at λ = 650 nm, P_{opt} is the optical power, k is the Boltzmann constant, T is the absolute temperature.

As was mentioned above we used thick single crystal CdTe substrates (d = 1 mm) for the fabrication of the $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ heterojunction solar cells under investigation. In the case of a thick absorber, Eq. (10) can be simplified:

$$\mathrm{TE}(W) = FT_{\mathrm{TiO_2}} \times \left[\frac{1+\dfrac{S}{D_p}\left(\alpha+\dfrac{2}{W}\dfrac{\varphi_0-qV_{oc}}{kT}\right)^{-1}}{1+\dfrac{S}{D_p}\left(\dfrac{2}{W}\dfrac{\varphi_0-qV_{oc}}{kT}\right)^{-1}} - \frac{\exp(-\alpha W)}{1+\alpha L_n}\right] - \frac{h\nu\left(B\exp[-\alpha_0(\varphi_o-qV_{oc})]+\dfrac{V_{oc}}{R_{sh}}\right)}{qP_{opt}} = 0. \quad (11)$$

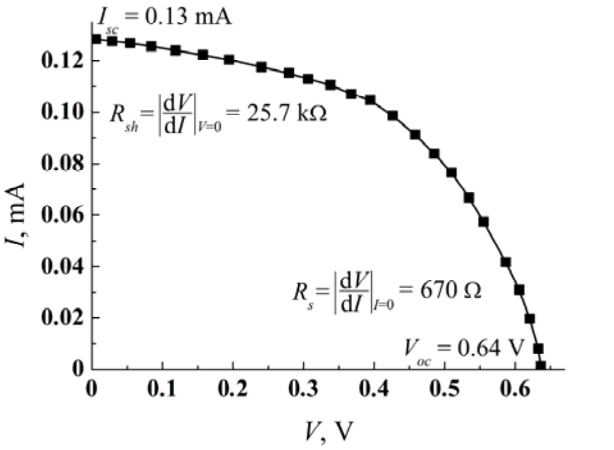

Fig. 6. The *I–V* characteristic of the solar cells illuminated by monochromatic light (λ = 650 nm, I_{opt} = 6 mW·cm^{-2}).

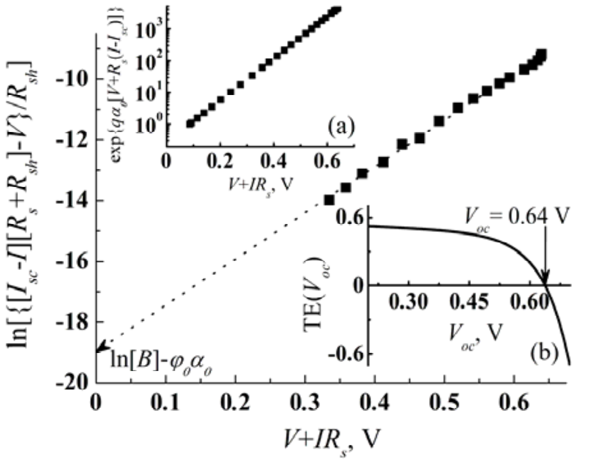

Fig. 7. The determination of the coefficients α_0 and B from the *I–V* characteristic of the $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ solar cells under monochromatic illumination (λ = 650 nm, I_{opt} = 6 mW·cm^{-2}). The inset (a) shows the ratio exp[$-\alpha_0(\varphi_0 - q(V + IR_s))$] / exp[$-\alpha_0(\varphi_0 - qIR_s)$]. The calculation of the open-circuit voltage V_{oc} is shown in the inset (b).

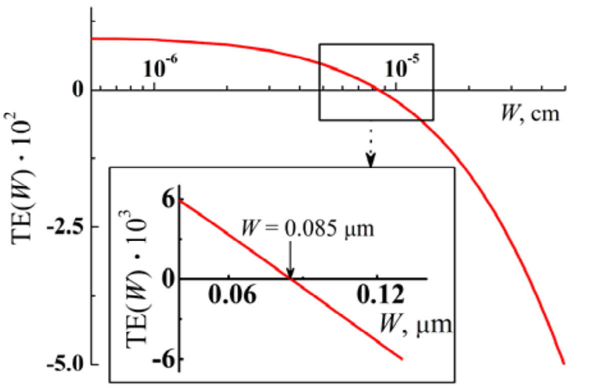

Fig. 8. The calculation of the width *W* of the space charge region of the $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ heterojunction solar cells by employing transcendental Eq. (11).

During the calculation using equation (11) at 295 K the shade factor F = 0.8 and the recombination velocity at the TiO$_2$/CdTe interface $S = 10^7\,\mathrm{cm\cdot s^{-1}}$. The high recombination velocity results from the high concentration of surface states at the heterojunction interface.

The measured value of the optical transmittance of the TiO$_2$ thin film deposited onto a quartz substrate simultaneously with the fabrication of the $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ heterojunctions is equal to T_{TiO2} = 0.34 at λ = 650 nm. The relatively low transmittance results from the high concentration of oxygen vacancies, which are responsible for low resistivity of pure TiO$_2$ thin films used in our study in order to decrease the series resistance of the $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ solar cells [21]. It is quite obvious that the doping of TiO$_2$ thin films is needed in order to obtain both highly conductive and transparent coatings.

The parameters of single crystal CdTe are taken from literature $D_n = 25\mathrm{cm^2\cdot s^{-1}}$ and $D_p = 2.5\mathrm{cm^2\cdot s^{-1}}$, $\tau_n = 10^{-9}\,\mathrm{s}$, $L_n = (\tau_n D_n)^{1/2}$ = 1.58 μm, α = 42000cm^{-1} [5, 22, 23].

The calculated value of the width W of the depletion region in the heterojunction solar cells under investigation is equal to $8.5\cdot10^{-6}\,\mathrm{cm}$ (Fig. 8). The concentration of uncompensated acceptors $N_A - N_D$ can be calculated by employing the following equation:

$$N_A - N_D = \frac{2\varepsilon_0\varepsilon_p[\varphi_0 - qV_{oc}]}{q^2W^2}, \qquad (12)$$

where ε_0 is the permittivity of free space and ε_p = 10.6 is the dielectric constant of CdTe. Finely we obtain the concentration of uncompensated acceptors in our single crystal CdTe substrate $N_A - N_D = 8.12\cdot10^{15}\mathrm{cm^{-3}}$ at 295 K, that is slightly higher than the concentration of free holes $p = 7.2\cdot10^{15}\mathrm{cm^{-3}}$ determined from electrical conductivity measurements at the same temperature [12].

It should be noted that the width W of the space charge region of the $\mathrm{n\text{-}TiO_2/p\text{-}CdTe}$ solar cells and thus the concentration of uncompensated acceptors $N_A - N_D$ were determined under light conditions. Their values may differ from that determined under dark conditions using the volt-capacitance technique due to the recharging traps within the space charge region under illumination.

4. Conclusions

Photoelectric properties of n-TiO$_2$/p-CdTe heterojunction solar cells, fabricated by means of TiO$_2$ thin film deposition onto freshly cleaved single crystal CdTe substrates using the DC reactive magnetron sputtering technique, were investigated under different light conditions: white light (I_{opt} = 100 mW·cm^{-2}) and monochromatic light (λ = 650 nm, I_{opt} = 6 mW·cm^{-2}).

The equation for the light *I-V* characteristic of the $n\text{-}TiO_2/p\text{-}CdTe$ solar cells was derived on the basis of the dominating current transport mechanism through the heterojunctions under forward biases (tunnel-recombination via defect states in the vicinity of the TiO_2/CdTe heterojunction) and in the presence of series and shunt resistance. The considerable effect of light dependent coefficients α_0 and B on photoelectric parameters of the $n\text{-}TiO_2/p\text{-}CdTe$ heterojunction solar cells, in particular open-circuit voltage V_{oc}, was quantitatively shown. Therefore, one should determine the mentioned coefficients under illumination in order to deal with an accurate analysis of photoelectrical properties of the $n\text{-}TiO_2/p\text{-}CdTe$ solar cells.

The width $W = 8.5 \cdot 10^{-6}$ cm of the space charge region of the $n\text{-}TiO_2/p\text{-}CdTe$ solar cells and consequently the concentration of uncompensated acceptors $N_A - N_D = 8.12 \cdot 10^{15}\text{cm}^{-3}$ were determined by employing the open-circuit method, which is based on the analysis of heterojunction solar cells illuminated by monochromatic light under open-circuit conditions.

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