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Light-dependent *I–V* characteristics of TiO₂/CdTe heterojunction solar cells

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Abstract

A new approach was proposed for the analysis of light current–voltage (I–V) characteristics of nonideal heterjunctions in the case of the dominating current transport mechanisms induced by multistep tunnel-recombination processes via interface states. I–V characteristics of the anisotype abrupt heterojunction n-TiO₂/p-CdTe were investigated under different light conditions. The values of the series R_s and shunt R_{sh} resistance, as well as those of the coefficients α and B, which quantitatively describe the dominating tunnel-recombination current transport mechanism, were established to be strongly dependent on light conditions.

1. Introduction

The main parameters of photoelectric devices are strongly dependent on dominating current transport mechanisms [1, 2]. It is quite obvious that conditions of charge carriers' transport should be investigated in detail, especially, in the case of semiconductor devices based on heterojunctions, due to a great variety of current transport mechanisms, which are inherent to them [3, 4].

As usual, current transport mechanisms in different photoelectric devices are investigated under dark conditions and then the obtained results are used, considering photoelectric parameters: short circuit current $I_{\rm sc}$, open circuit voltage $V_{\rm oc}$, fill factor FF and efficiency η . Unfortunately this approach is not always valid. In the case of solar cells based on different heterojunctions and metal—oxide—semiconductor junctions current transport mechanisms may be strongly dependent on light conditions [5, 6]. Therefore, the coefficients, which determine the current transport mechanism in a heterojunction solar cell, should be determined under light conditions in order to carry out the quantitative analysis of photoelectric properties of a heterojunction solar cell with high accuracy and reliability.

There are a number of papers dedicated to the preparation and characterization of $TiO_2/CdTe$ heterojunctions [7–11],

which show that these heterojunctions can be used in photovoltaics.

The aim of this work is to adapt the recently proposed technique for the analysis of light-dependent current transport mechanisms [12] to the anisotype heterojunctions n-TiO₂/p-CdTe and to investigate their light-dependent I-V characteristics under different light conditions.

2. Experimental part

The CdTe single crystals with p-type conductivity were grown by the Bridgman method at low cadmium vapor pressure ($P_{\rm Cd}=0.02$ bar) in Chernivtsi National University. The values of specific electrical conductance and majority carriers concentration at 295 K for these crystals were measured to be $\sigma=8.9\times10^{-2}~\Omega^{-1}~{\rm cm}^{-1}$ and $\rm p=7.2\times10^{15}~{\rm cm}^{-3}$, respectively.

The fabrication of the n-TiO $_2$ /p-CdTe heterojunctions was carried out by the deposition of TiO $_2$ thin films onto freshly cleaved single crystal CdTe substrates (1 1 0) with dimensions $5 \times 4 \times 1$ mm by means of DC reactive magnetron sputtering of a pure Ti target using a universal coating system Laybold-Heraeus L560.

During the deposition process, the partial pressures of argon and oxygen were equal to 7×10^{-3} and 2×10^{-4} mbar, respectively (P_{O2} : $P_{Ar} = 1:35$). The magnetron power was 350 W. The substrate temperature was 573 K. The deposition process lasted for 20 min.

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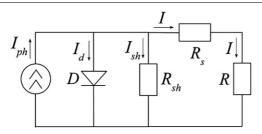


Figure 1. The equivalent circuit of a n-TiO₂/p-CdTe heterojunction.

The obtained TiO_2 thin film possessed n-type of conductivity due to oxygen vacancies [13]. The measured values of specific electrical conductance and majority carriers concentration at 295 K for the TiO_2 thin films were $\sigma = 0.71~\Omega^{-1}~\text{cm}^{-1}$ and $n = 4.8 \times 10^{17}~\text{cm}^{-3}$, respectively.

The frontal point indium contacts to the heterojunctions were prepared by means of the thermal evaporation technique. Before the back contacts were prepared, the back surface of the heterojunctions (p-CdTe) were exposed by a monopulse of a powerful ruby laser with the wavelength $\lambda=0.694~\mu m$ and pulse duration $\tau=1.2$ ms in order to create a p+-layer due to additionally generated cadmium vacancies on the back surface. The Au and Cu layers were successively deposited onto the laser-treated back surface by means of reduction from aqueous solutions of gold chloride and copper vitriol, respectively.

The prepared heterojunction solar cells had the following photoelectrical parameters under 100 mW cm⁻² illumination: the open-circuit voltage $V_{\rm oc} = 0.69$ V, the short-circuit current $J_{\rm sc} = 6$ mA cm⁻², the fill factor FF = 0.42. Also a wide spectral region of the photosensitivity of the TiO₂/CdTe solar cells (350–850 nm) was shown in our previous work [11].

The light *I–V* characteristics of the n-TiO₂/p-CdTe heterojunction were measured using a SOLARTRON SI 1286, SI 1255 complex. The sources of monochromatic light and white light 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.

3. Theory

The analysis of the anisotype heterojunctions n-TiO₂/p-CdTe will be carried out in the scope of the generally accepted equivalent circuit in the presence of series $R_{\rm s}$ and shunt $R_{\rm sh}$ resistance (figure 1). One can express the external current I as follows: $I = I_{\rm ph} - I_{\rm d} - I_{\rm sh}$, where $I_{\rm ph}$ is the photocurrent, $I_{\rm d}$ is the diode current and $I_{\rm sh}$ is the current through the shunt resistance $R_{\rm sh}$.

Having analyzed the I-V characteristics of the heterojunctions measured at different temperatures the dominating current transport mechanism was established to be multistep tunnel-recombination via interface states within the forward biases 3kT/q < V < 0.7 V [11]:

$$I = B \exp(-\alpha(\varphi_0 - qV)), \tag{1}$$

where coefficients α and B are equal to 9.5 and 9 × 10⁻⁵, respectively at 295 K; V is the applied voltage φ_0 is the height of the potential barrier $\varphi_0 = qV_{\rm bi} \approx 0.7$ eV at 295 K, where $V_{\rm bi}$ is the built-in potential.

Hereafter the I-V charactersistcs will be analyzed within the fourth quadrant; therefore the heterojunction solar cells will be considered at forward biases $0 < V < V_{\rm oc}$. Since the maximum value of the open circuit voltage of the n-TiO₂/p-CdTe solar cells ($V_{\rm oc}=0.69~V$ [11]) is less than 0.7 V the expression for the diode current $I_{\rm d}$ is governed by the mentioned above tunnel-recombination current transport mechanism:

$$I_{\rm d} = B \exp\{-\alpha[\varphi_0 - q(V + IR_{\rm s})]\},\tag{2}$$

where the applied voltage V was replaced by $V + IR_s$ in order to take into consideration the effect of the series resistance R_s . Taking into account (2) one can write the following expression for the light I-V characteristic of a n-TiO₂/p-CdTe heterojunction [14]:

$$I = I_{\rm ph} - B \exp\{-\alpha[\varphi_0 - q(V + IR_{\rm s})]\} - \frac{V + IR_{\rm s}}{R_{\rm sh}}.$$
 (3)

It is known that the values of the coefficients related to current transport mechanisms (for example, saturation current I_0 and ideality coefficient n) in different heterojunctions may depend on light intensity and wavelength [5, 6]. It is quite natural to assume that the coefficients B and α , which quantitatively describe the dominating multistep tunnel-recombination current mechanism in our heterojunctions, also depend on light conditions. The values of the above mentioned coefficients can be determined from the direct branch of the light I-V characteristic of a n-TiO₂/p-CdTe solar cell. In order to show this let us write the expression for the light I-V characteristic (3) under short circuit condition ($I=I_{sc}$, V=0):

$$I_{\rm sc} = I_{\rm ph} - B \exp\{-\alpha[\varphi_0 - qI_{\rm sc}R_{\rm s}]\} - \frac{I_{\rm sc}R_{\rm s}}{R_{\rm sh}}.$$
 (4)

If we express the photocurrent I_{ph} from the last equation and substitute it into (3), we shall obtain the following equation:

$$\frac{[(I_{\rm sc} - I)(R_{\rm s} + R_{\rm sh}) - V]}{R_{\rm sh}} = B\{\exp[-\alpha(\varphi_0 - q(V + IR_{\rm s}))].$$

$$-\exp[-a(\varphi_0 - qI_{\rm sc}R_{\rm s})]\}. \tag{5}$$

When the following inequality is valid $\exp[-\alpha(\varphi_0 - q(V + IR_s))] \gg \exp[-\alpha(\varphi_0 - qIR_s)]$, equation (5) becomes a linear dependence in the semilogarithmic coordinates $\ln[\{(I_{sc} - I)\}(R_s + R_{sh}) - V\}/R_{sh}]$ versus $(V + IR_s)$ as is seen from equation (6):

$$\ln\left[\frac{\{[I_{\rm sc} - I[R_{\rm s} + R_{\rm sh}] - V\}}{R_{\rm sh}}\right] = \ln[B] - \varphi_0 \alpha + q\alpha[V + IR_{\rm s}]. \tag{6}$$

One can easily determine the actual value of the coefficient α from the slope of the linear dependence (23):

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

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

$$B = \exp\left[\left.\varphi_0\alpha + \ln\left[\frac{\{[I_{sc} - I][R_s + R_{sh}] - V\}}{R_{sh}}\right]\right|_{[V + IR_s] = 0}\right].$$
(8)

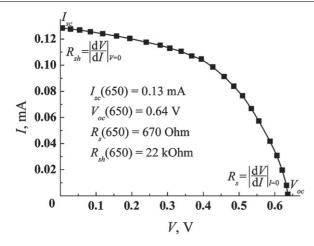


Figure 2. The light I-V characteristic of the n-TiO₂/p-CdTe heterojunction solar cells under the monochromatic illumination ($\lambda = 650 \text{ nm}$, $I_{\text{opt}} = 6 \text{ mW cm}^{-2}$).

It is worth noting that the series R_s and shunt R_{sh} resistance also depend on light conditions [5]. Their actual values can be easily determined from the same light I-V characteristic using the following conditions [15]:

$$R_{\rm s} = \left| \frac{\mathrm{d}V}{\mathrm{d}I} \right|_{I=0}, \quad R_{\rm sh} = \left| \frac{\mathrm{d}V}{\mathrm{d}I} \right|_{V=0}.$$
 (9)

4. Results and discussions

In order to show the effect of light conditions on the I–V characteristics of the anisotype heterojunctions n-TiO₂/p-CdTe we shall apply the described above method for the determination of the coefficients of α and B under different light conditions: monochromatic light and white light with different intensities.

Figure 2 shows the I-V characteristic of the n-TiO₂/p-CdTe heterojunctions under the monochromatic illumination with the wavelength 650 nm and intensity $I_{\text{opt}} = 6 \text{ mW cm}^{-2}$.

The actual values of the series $R_{\rm s} = 670 \ \Omega$ and shunt $R_{\rm sh} = 2.57 \times 10^4 \ \Omega$ resistance were determined from the light I-V characteristic using conditions (9).

Let us plot this I-V characteristic in the semilogarithmic coordinates $\ln[\{(I_{sc}-I))(R_s+R_{sh})-V\}/R_{sh}]$ versus $(V+IR_s)$ (figure 3).

One can see the linear dependence, which is governed by equation (6). Its slope provides us with the value of the coefficient $\alpha(650) = 15.2 \, \mathrm{eV^{-1}}$. At the forward biases less than 0.35 V experimental points deviate from the linear dependence due to the failure of the inequality mentioned above $\exp[-\alpha(\varphi_0 - q(V + IR_s))] \gg \exp[-\alpha(\varphi_0 - qIR_s)]$ (the inset of figure 3).

The second coefficient $B(650) = 2.4 \times 10^{-4}$ A was determined by the extrapolation of the linear dependence toward its interception with the current axis (figure 3) using equation (8).

The 4 light-dependent parameters $R_s(650)$, $R_{sh}(650)$, $\alpha(650)$ and B(650) were determined from the I-V characteristic of the n-TiO₂/p-CdTe heterojunctions under the monochromatic illumination (figure 2).

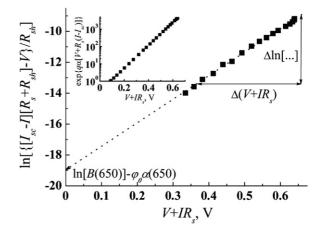


Figure 3. The determination of the coefficients $\alpha(650)$ and B(650) from the I-V characteristic of the heterojunctions under the monochromatic illumination. The inset shows the ratio $\exp[-\alpha(\varphi_0 - q(V + IR_s))]/\exp[-\alpha(\varphi_0 - qIR_s)]$ as a function of forward bias.

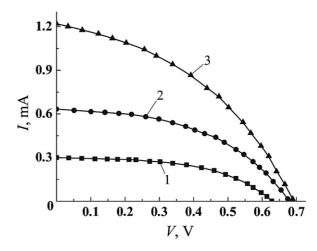


Figure 4. Light *I–V* characteristics of the n-TiO₂/p-CdTe heterojunction solar cells under white light illumination: 1–25 mW cm⁻², 2–50 mW cm⁻², 3–100 mW cm⁻².

Now let us analyze the light I–V characteristics of the heterojunctions measured under white light illumination with different intensities (figures 4 and 5).

It is seen from figure 5 that the I-V characteristics can be well extrapolated by straight lines with different slopes in the semilogariphm coordinates $\ln[\{(I_{sc} - I)(R_s + R_{sh}) - V\}/R_{sh}]$ versus $(V + IR_s)$. According to expression (8) this fact results in different values of the coefficient α under different light intensities (the inset (b) of figure 5). The coefficient B was established to be also dependent on light intensity (the inset (c) of figure 5).

The observed light dependence of the tunnel-recombination current transport mechanism can be caused by the absorption of incident light by interface and bulk states in the vicinity of $TiO_2/CdTe$ interface. The change of the distribution of ionized acceptors results in the change of the width of space charge region and the shape of potential barrier. Coefficient α is known to be dependent on the shape of potential barrier; coefficient B is proportional to the density of interface states [4, 16–18]. Since interface states,

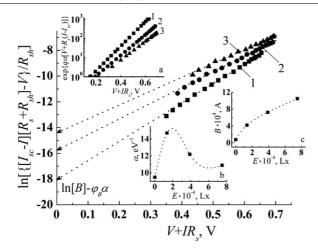


Figure 5. The determination of the coefficients α and B from the I-V characteristics of the heterojunctions under white light illumination: $1-25 \text{ mW cm}^{-2}$, $2-50 \text{ mW cm}^{-2}$, $3-100 \text{ mW cm}^{-2}$. The insets show the following: (a) the ratios $\exp[-\alpha(\varphi_0 - q(V + IR_s))]/\exp[-\alpha(\varphi_0 - qIR_s)]$ as the functions of forward bias under different intensities, (b) the dependence of α on light intensity, (c) the dependence of B on light intensity. The dashed lines are a guide for the eye.

Table 1. Light-dependent electric parameters of the heterojunction.

Light conditions	$R_{\rm s}$, Ω	$R_{\rm sh}$, k Ω	α , eV ⁻¹	$\beta \times 10^4$, α
Dark [8]	780	895	9.5	0.9
ML ^a 650 nm	670	25.7	15.2	2.4
$\mathrm{WL^b}\ 25\ \mathrm{mW}\ \mathrm{cm}^{-2}$	510	16	14.7	4.26
$\mathrm{WL}~50~\mathrm{mW}~\mathrm{cm}^{-2}$	290	11	12.2	7.24
$\frac{\mathrm{WL}\ 100\ \mathrm{mW\ cm^{-2}}}{\mathrm{WL}\ 100\ \mathrm{mW}\ \mathrm{cm^{-2}}}$	180	2.2	10.9	10.5

^a ML-monochromatic light.

usually, create both shallow and deep levels within band gap [19–23], the charge state of heterojunction interface, as well as coefficients α and B, should be light (wavelength and intensity) dependent as is in fact seen (figures 3 and 5).

The values of the light-dependent electric parameters (R_s , R_{sh} , α and B) are given in table 1 in order to summarize the effect of the light conditions on the I-V characteristics of the anisotype heterojunctions n-TiO₂/p-CdTe.

5. Conclusions

Light I-V characteristics of anisotype photosensitive heterojunctions n-TiO₂/p-CdTe were considered in terms of the generally accepted equivalent circuit in the presence of series R_s and shunt R_{sh} resistance. The diode current I_d through the heterojunctions was considered in the scope of the tunnel-recombination model [11].

The previously proposed technique for the analysis of light-dependent I–V characteristics [12] was adapted to the dominating current transport mechanism induced by multistep

tunnel-recombination processes via interface states. It was applied in order to analyze the I-V characteristics of the n-TiO₂/p-CdTe heterojunction solar cells under different light conditions: monochromatic light ($\lambda = 650$ nm, $I_{\rm opt} = 6$ mW cm⁻²) and white light with different intensities (25, 50 and 100 mW cm⁻²).

The values of the coefficients α and B, which quantitatively describe the dominating tunnel-recombination current transport mechanism, were established to be strongly dependent on light conditions (figure 5 and table 1). The observed light dependence of the tunnel-recombination current transport mechanism can be caused by the absorption of incident light by interface and bulk states in the vicinity of a $TiO_2/CdTe$ heterojunction interface.

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^bWL-white light.