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Open-Circuit Voltage of an Illuminated Nonideal Heterojunction

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Abstract—The possibility of using the model of tunneling-recombination transport for calculating the photovoltage of an illuminated nonideal heterojunction is demonstrated. The technique of photoexcitation with light of varying spectral composition is used, and the difference in the behavior of the dependence of the photovoltage on the illumination is explained. The heterojunction photovoltage is calculated taking into account the predominance of the tunneling-recombination transport mechanism in the barrier region and modification of the shape of the potential barrier during illumination. It is shown that the dependences calculated at various illumination levels agree with those obtained experimentally.

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1. INTRODUCTION

In [1] we proposed the method of using the Mott model [2] (tunnel-hopping conductivity developed for noncrystalline materials) for describing the conductivity of inhomogeneous structures, for example, that in the space-charge region (SCR) of a nonideal heterojunction. How to take into account the effect of processes occurring at the heteroboundary of such structures for calculation of the current flow and the *I–V* characteristic is also shown. At the same time, it was shown in [3, 4] how the illumination of a nonideal heterojunction can modify the SCR width in the heterojunction and the potential-barrier shape, thus affecting its conductivity [5]. All of this must be taken into account when determining the photovoltage of an illuminated nonideal heterojunction.

2. DETERMINATION OF THE PHOTOVOLTAGE OF AN ILLUMINATED NONIDEAL HETEROJUNCTION

For definiteness' sake, we further consider the CdS–Cu_2S heterojunction, which represents a sharply asymmetric structure in which almost the entire SCR is localized in high-resistivity CdS. According to [6], the expression for the *I–V* characteristic of the illuminated heterojunction has the form

$$j = n_c \exp\left(-\frac{\varphi_0}{kT}\right) e v_\delta \frac{s_\delta \exp\left(\frac{eU}{kT} - 1\right)}{v_\delta + s_\delta} - \frac{e v_\delta L\gamma\eta}{v_\delta + s_\delta}. \quad (1)$$

Here, n_c is the concentration of majority carriers in the quasineutral region of CdS, φ_0 is the barrier height, s_δ is the surface-recombination rate, v_δ is the drift rate at the heteroboundary, L is the incident-energy density, γ is the collection coefficient in Cu_2S (disregarding losses at the heteroboundary), and η is the quantum yield. It should be kept in mind that it was only the thermal-diffusion mechanism of current transfer that was considered in [7]; i.e., tunnel-hopping mechanisms were disregarded in Eq. (1).

From formula (1), it is easy to obtain the expression for the open-circuit voltage U_{oc} of the illuminated heterophotocell assuming that $j = 0$:

$$\frac{v_\delta}{v_\delta + s_\delta} L\gamma\eta = \left(\frac{v_\delta}{v_\delta + s_\delta} L\gamma\eta + e v_\delta n_0\right) \times \frac{s_\delta e^{\frac{\varphi_0}{kT}}}{v_\delta + s_\delta}\left(e^{\frac{U_{oc}}{kT}} - 1\right). \quad (2)$$

Here, the left-hand side determines the flux of electrons photogenerated in the Cu_2S region through the interface, and the right-hand side, the reverse thermal-diffusion current. The calculation shows that the following inequality is always fulfilled with increasing stimulating-light intensity up to solar light intensity for the CdS–Cu_2S heterojunction:

$$\frac{v_\delta}{v_\delta + s_\delta} L\gamma\eta \ll e v_\delta n_0. \quad (3)$$

Taking into account (3), after simple transformations, it is easy to obtain an obvious expression for determining U_{oc} from Eq. (2). Taking into account that

$n_0 = N_D$ in the CdS quasineutral region and designating $L\gamma\eta = j_0$, we obtain

$$U_{oc} = \varphi_0 + kT\ln\left(\frac{j_0}{es_\delta N_D} + e^{\frac{\varphi_0}{kT}}\right). \quad (4)$$

From (4), it can be seen that the open-circuit photovoltage of the illuminated sample is independent of the parameter v_δ (hence, it is independent of the shape of the potential barrier), and is determined only by the generation rate of carriers in Cu_2S and their recombination rate at the heteroboundary.

The value of U_{oc} is determined from the condition of equality of two carrier fluxes, i.e., from Cu_2S to CdS and the reverse flux from CdS to Cu_2S, caused by various mechanisms of carrier transport through the barrier. The mechanisms can be both thermally activated and tunneling in character. Introducing the tunneling-recombination currents (j_T) flowing through the potential barrier in the model and taking into account inequality (3), we transform(2) to a more general form:

$$\frac{v_\delta}{v_\delta + s_\delta}L\gamma\eta = ev_\delta n_0\frac{s_\delta e^{\frac{\varphi_0}{kT}}}{v_\delta + s_\delta}\left(e^{\frac{U_{oc}}{kT}} - 1\right) + j_T. \quad (5)$$

Now the right-hand side determines both the reverse thermal-diffusion and tunneling-recombination currents. To calculate j_T caused by the motion of carriers along localized states and their recombination at the interface, it is necessary to specify the barrier height $\varphi_0 - U_{oc}$ and its width ω, and also the dependence φ(*x*), which, according to [3, 4], under illumination conditions can dramatically differ from quadratic law, which greatly affects the value of v_δ determining the left-hand side of (5).

Under conditions of the excitation of wide-gap CdS in which the barrier is localized, it is possible to determine these parameters unambiguously, specifying the values of the dark capacitance C_D and junction photocapacitance C_L. When carrying out the experiment and for calculations, it is convenient to use the dependences $v_\delta(C_D, U_{oc})$, $U_{oc}(C_L)$, $j_T(C_L, U_{oc})$. If we assume that the cell is irradiated with only long-wavelength light, then the specified parameters are only determined the decrease in the barrier height to a value of $\varphi_0 - U_{oc}$ for its arbitrary intensities and a certain decrease in its width related to it. The estimated calculations show that, for $U_{oc} < 0.7$ V (valid to solar-light illumination), the tunneling-recombination current j_T exceeds the thermal-diffusion component by several orders of magnitude.

This means that, for low stimulating-light intensities, (5) for determining U_{oc} in a nonideal heterojunction is simplified to the form

$$L\gamma\eta\frac{v_\delta(U, C_\Phi)}{v_\delta(U, C_\Phi) + s_\delta} = j_T(U, C_\Phi). \quad (6)$$

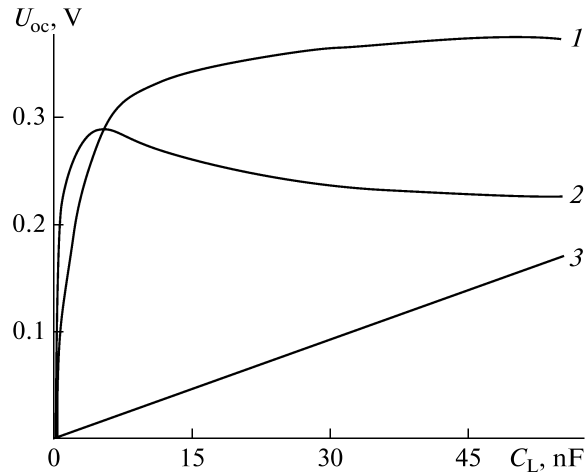

Fig. 1. Experimental dependences of the open-circuit voltage of illuminated CdS–Cu_2S photocells on the value of the photocapacitance C_L depending on the intensity of stimulating white light.

As was noted above, the tunneling currents and recombination at the interface of the nonideal heterojunction significantly affect its photoelectric properties. The problem of photovoltage losses is relatively complex because here it is necessary to take into account the decrease in the free-carrier flux, which intersects the heteroboundary due to recombination, instead of just the flux itself, and also efficient shunting of the barrier by the tunneling currents.

3. EXPERIMENTAL RESULTS

In Fig. 1, we show the experimentally obtained dependences of the open-circuit voltage for the illuminated CdS–Cu_2S photocells on the photocapacitance, which directly depends on the illumination of the samples by white light [5]. The samples under investigation differed in terms of the technological parameters of the heterojunction formation; in particular, the film-deposition time and the substrate temperature were varied when depositing the base CdS layer. These differences caused the division of the measured dependences into three characteristic types. Some cells showed saturation of the open-circuit voltage during illumination for relatively low values of the photocapacitance and, correspondingly, for low white-light intensities (Fig. 1, curve *1*). For a number of samples, the illuminated-cell voltage, rapidly achieving the largest value, somewhat decreased with increasing capacitance depending on the light intensity (Fig. 1, curve *2*). Sometimes we observed a close-to-linear increase in U_{oc} (Fig. 1, curve *3*). As was shown previously, in the case of the predominance of tunneling-recombination mechanisms of current flow determining U_{oc}, its value greatly depends on the

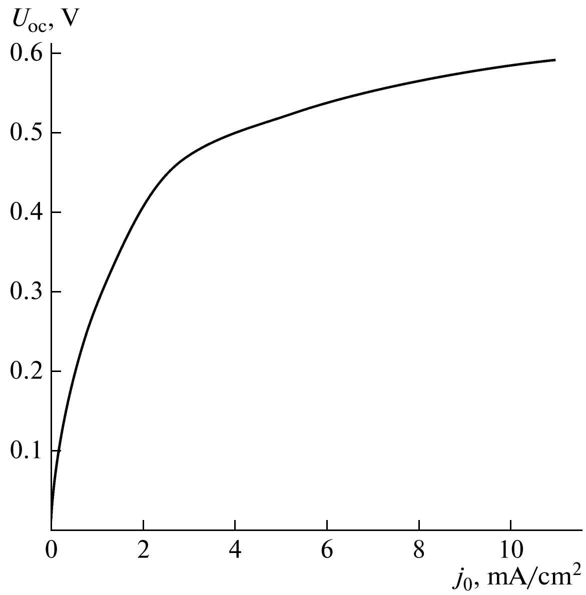

Fig. 2. Dependence of the open-circuit photovoltage on the intensity of illumination with long-wavelength light ($\lambda > 950$ nm). The intensity is proportional to the silicon-photocell photocurrent.

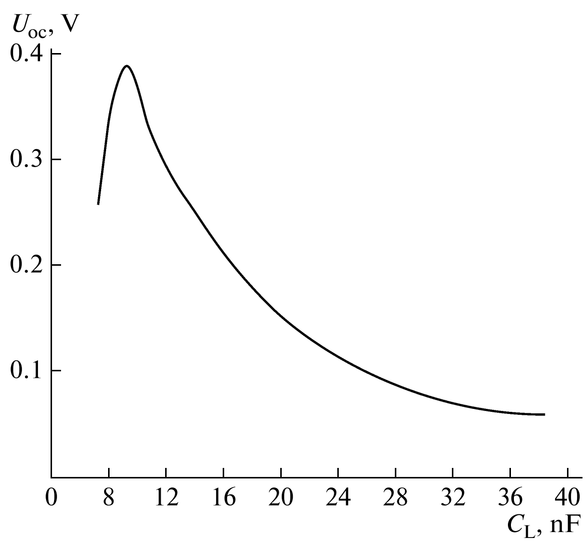

Fig. 3. Dependence of the open-circuit photovoltage generated by constant long-wavelength light on the photocapacitance C_L depending on the intensity of additional short-wave illumination ($\lambda < 520$ nm).

parameters of the potential barrier of the heterostructure, e.g., the barrier height, width, and shape.

An increase in the white-light intensity results in the occurrence of two simultaneous processes, i.e., a linear ($j_0 = L\gamma\eta$) increase in the generation of carriers in Cu_2S due to long-wavelength light and modification of the shape of the potential barrier due to the short-wavelength spectral component. All this makes interpretation difficult and complicates numerical simulation of the experimental results.

In connection with this, we used an experimental approach consisting in the separate consideration of factors and mechanisms determining the dynamics of the photovoltage. In the beginning, the photocells were illuminated with only the long-wavelength component ($\lambda > 950$ nm), and the dependence of the illuminated-cell open-circuit voltage on the light intensity was determined. In this case, we excluded the excitation of wide-gap CdS and, correspondingly, the barrier parameters varied insignificantly (only due to a decrease in its height to a value of $\varphi_0 - U_{oc}$ in the illuminated-cell-photovoltage mode). One of the typical experimental curves is shown in Fig. 2. The obtained dependences revealed no saturation or decrease in U_{oc} with increasing intensity of long-wavelength illumination, as was observed for white light (Fig. 1, curves *1* and *2*).

Then we carried out simultaneous illumination of the sample with long-wavelength light of constant intensity and with varying-intensity short-wavelength light. In this case, the carrier-photogeneration rate in Cu_2S was invariable, and the value of U_{oc} was determined only by the modification of the potential-barrier shape. The dependence characteristic of this technique is shown in Fig. 3. The obtained experimental curve shows a fast initial increase, a peak, and, then, a slow decrease in U_{oc}.

4. ANALYSIS AND DISCUSSION OF RESULTS

In the analysis of the experimental results, we used the above model for tunneling-recombination transport in the illuminated heterojunction. This model, with the mechanism of the transport of nonequilibrium carriers from Cu_2S through the heteroboundary taken into account, enables us to carry out rather accurate numerical simulation of the processes determining the open-circuit photovoltage of an illuminated nonideal CdS–Cu_2S heterostructure.

The solution of the problem of determining U_{oc} for a nonideal heterojunction is reduced to the numerical search for such a value at which expression (6) is satisfied for the specified illumination level L and barrier shape (which depends on the dark capacitance and the photocapacitance, as well as on the value of U). The desired U value is that of the illuminated-cell open-circuit photovoltage U_{oc}.

Interpretation and numerical simulation of the obtained results were carried out separately for the case of photocell illumination with only long-wavelength light, in the presence of additional short-wavelength illumination and for junction illumination with undecomposed wide-range light.

4.1 Illumination of the Photocell with only Infrared Light ($\lambda > 950$ nm)

Varying the light illumination intensity, in this case, will vary only the carrier-generation rate ($L\gamma\eta$) in Cu_2S instead of the potential-barrier shape (only its width somewhat varies due to internal bias). This means that the value of the effective shunting resistance of the junction varies only due to lowering of the barrier by the value of U_{oc} with increasing infrared-light intensity. Therefore, to calculate j_T, it is possible to use the technique developed for calculating the dark tunneling-recombination currents [1]. The change in the coefficient of carrier separation at the heteroboundary, which is determined by the dependence of v_δ on the bias, is also insignificant. All this determines the character of the dependence $U_{oc}(L)$. This problem was solved numerically.

The dependences of U_{oc} on the value of $j_0 = L\gamma\eta$ shown in Fig. 4 are calculated for the following values of the parameters determining j_T and the value of $\frac{v_\delta}{v_\delta + s_\delta}$:

$$C_D = 12.5 \text{ nF}, \quad s_\delta = 3000 \text{ m/s}, \quad N_0 = 10^{27} \text{ m}^{-3},$$
$$T = 300 \text{ K}, \quad \text{and} \quad E_0 = 0.8 \text{ eV}.$$

Such values of parameters N_0 and E_0 describing the distribution of localized states in the band gap along which tunnel-hopping transport occurs give the best agreement between the calculated and experimental temperature and I–V dependences of j_T. The presented values of the dark capacitance and the surface-recombination rate of free carriers at the heteroboundary are typical of the structure under investigation [8]. These values were used for all curves shown in Fig. 4. For the value $N_r = 10^{18}$ m^{-2}, the calculated curve well coincides with the experimental curve shown in Fig. 2.

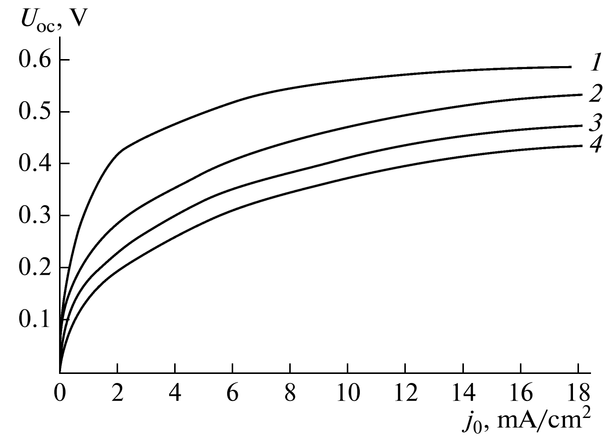

Fig. 4. Dependences of U_{oc} on j_0 calculated for different values N_r of the concentration of surface recombination centers at the heteroboundary: 10^{18}, 2×10^{18}, 10^{19}, 10^{20} m^{-2} (curves *1*–*4*, respectively).

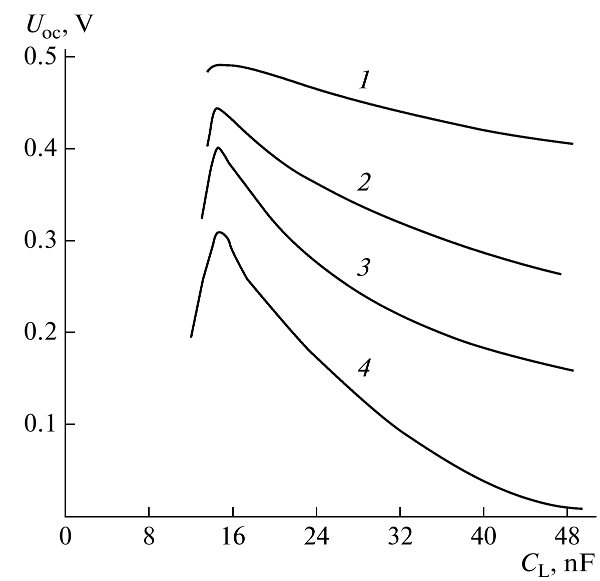

Fig. 5. Dependences of U_{oc} on the photocapacitance value calculated at various concentrations N_r of the surface recombination centers: 10^{18}, 2×10^{18}, 10^{19}, 10^{20} m^{-2} (curves *1*–*4*, respectively). Curve *4* is calculated for the case of restriction of j_T only by transport in the SCR.

4.2 Presence of Additional Short-Wavelength Illumination Affecting the Width and Potential-Barrier Shape in CdS

We assume that the intensity of the long-wavelength light remains constant (in (6) $L\gamma\eta = \text{const}$), and only the intensity of the short-wavelength illumination, which is specified via the heterojunction photocapacitance C_L, varies in the calculations. In contrast to the previous case, in the calculations, it is now necessary to find the potential-barrier shape corresponding to it for each value of photocapacitance (for the short-wavelength light intensity) [3, 4]. However, it is necessary to take into account in this case that the barrier height amounts to the value of $\varphi_0 - U_{oc}$ in the open-circuit mode.

The calculations were carried out at the same parameters as in the case of Fig. 4. The value of $j_0 = L\gamma\eta$ determined only by the generation constant in Cu_2S was taken to be 10 mA/cm^2, and the photocapacitance varied within the range 12.5–50 nF. The same as previously, the calculations were carried out for several values of the surface concentration N_r of recombination centers at the heteroboundary determining its effective conductivity. The calculated dependences $U_{oc}(C_L)$ are shown in Fig. 5. Their qualitative agreement with the experimental curve is clearly seen in Fig. 3.

The sharp initial increase in the open-circuit voltage upon a small increase in the photocapacitance is

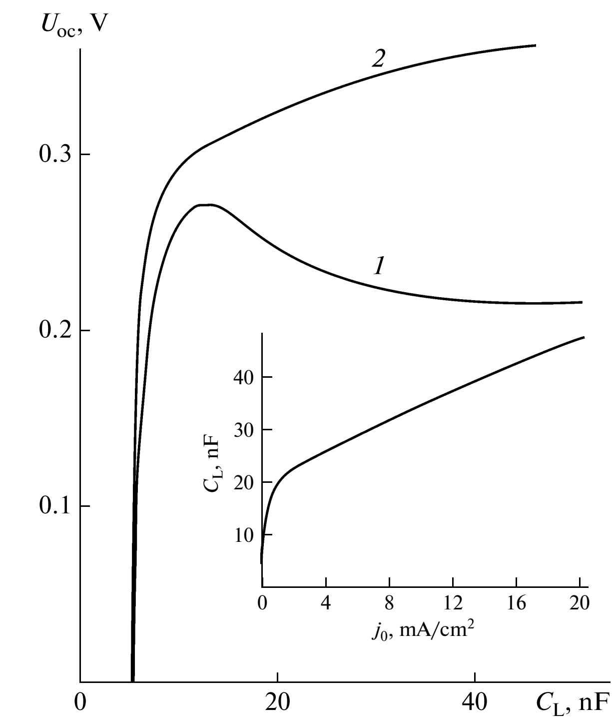

Fig. 6. Calculated dependence of U_{oc} for a heterophotocell upon illumination with white light on its photocapacitance for two values of $N_r = 10^{18}$ cm^{-2} (curve *1*) and $N_r = 10^{16}$ cm^{-2} (curve *2*). The inset shows the experimental dependence of the photocapacitance on $j_0 = L'\gamma\eta$ (L' is the white-light intensity) measured for a nonideal heterostructure CdS–Cu_2S.

caused by an increase in the flux of carriers generated in Cu_2S through the interface due to a decrease in their recombination at the heteroboundary with increasing $\left.\frac{d\varphi}{dx}\right|_{x=0}$. Thus, a decrease in recombination results in a fast increase in the left-hand side of expression (6) for a relatively small increase in j_T. Therefore, equality (6) is satisfied at higher values of U than in the absence of additional illumination. The further increase in the photocapacitance and, thus, the value of v_δ results in the fact that the coefficient $\frac{v_\delta}{v_\delta + s_\delta}$ at $v_\delta \gg s_\delta$ tends to unity. This means that almost all carriers generated by long-wavelength light in narrow-gap Cu_2S and those that approached the interface cross it and enter into the quasineutral CdS region forming the photovoltage. Since the generation in Cu_2S is constant, the further increase in the photocapacitance caused by increasing the intensity of short-wavelength illumination results in no appreciable increase om the carrier flux from Cu_2S through the heteroboundary and no increase in U_{oc}. However, due to the continuing decrease in the potential-barrier width, the value of the reverse tunneling-recombination current j_T increases [5]. This results in fulfillment of equality (6) at lower values of U; therefore, U_{oc} starts to decrease with a further increase in the photocapacitance.

4.3. The Case of Irradiation of the Photocell with Wide-Range White Light

When calculating the dependence of the open-circuit voltage on the intensity of undecomposed light (such a case is implemented in practice), it is necessary to take into account the following. In contrast to the two above cases, in equality (6)both the carrier-generation rate $L\gamma\eta$ in Cu_2S (due to a change in the long-wavelength-light component) and the photocapacitance (due to a change in the short-wavelength component), on which depend the coefficient of carrier separation at the heteroboundary and the value of j_T, vary. After determining the experimental dependence $C_L = C_L(L')$, where L' is the white-light intensity (see inset in Fig. 6), upon calculation of the illuminated-cell photovoltage, it is possible to associate the value of C_L to each value of L' or $j_0 = L'\gamma\eta$. Thus the obtained dependences of the illuminated-cell voltage on the photocapacitance calculated at various values of the surface concentration (N_r) of recombination centers at the heteroboundary (the capture cross section of these centers was assumed, as before, to be equal to 10^{-19} m^2) are shown in Fig. 6.

If the concentration is reasonably high ($N_r = 10^{18}$ m^{-2}), the recombination rate proves to be so high that, as calculations show, the current j_T flowing through the heterojunction is limited only by hopping conductivity in the SCR. With increasing intensity of the stimulating white light L', the barrier width of the heterojunction decreases, which results in increasing photocapacitance and tunneling current j_T. It can lead to a faster increase in the right-hand side of (6) in comparison with an increase with L' in its left-hand side and, hence, to decreasing U_{oc} with increasing photocapacitance (Fig. 6, curve *1*).

For the concentration $N_r = 10^{16}$ m^{-2}, the rate of surface recombination is lower, and the interface begins to greatly limit the current j_T. As at the heteroboundary, the process of the recombination of charge carriers moving along localized states is independent of the barrier parameters, the tunneling-recombination current j_T increases with increasing photocapacitance more weakly than in that case, when this current is determined only by the SCR conductivity. In this case, with increasing L', the right-hand side in equality (6) increases more weakly than the left-hand side, and no U_{oc}-decreasing portion is observed (Fig. 6, curve *2*). At the same time, there occurs significant restriction in the open-circuit photovoltage and the tendency of this value to saturation, which is also observed experimentally (Fig. 1, curve *1*). As can be seen in Fig. 6, the calculated curves well correspond to the experimentally obtained dependences shown in Fig. 1 (curves *1* and *2*).

5. CONCLUSION

Thus, it is shown that the dependence of the open-circuit photovoltage of a nonideal heterojunction under illumination conditions can be calculated taking into account, first of all, the tunneling-recombination leakage currents dependent on the potential-barrier shape and the recombination rate at the heteroboundary. In this case, a decrease in the photovoltage of photocells based on nonideal heterostructures can be explained and simulated taking into account the tunneling-recombination-transport model. The main sources of loss are the mechanisms related to hopping conductivity over localized states in the space-charge region. It is shown that a decrease in the surface concentration N_r of the recombination centers results in decreasing photovoltage losses.

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