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Space charge region recombination, non-radiative exciton recombination and the band-narrowing effect in high-efficiency silicon solar cells

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Abstract. An expression for finding the dependence of narrowing the bands in silicon ΔE_g on the level of illumination from the intrinsic absorption band (or short-circuit current) has been proposed. This expression is used to find experimental values of ΔE_g in high-efficient silicon solar cells. The dependence $\Delta E_g(J)$ or dependence $\Delta E_g(J_I)$, where J_I is the short-circuit current density, has been rebuilt into the $\Delta E_g(\Delta n_{OC})$ dependence, where Δn_{OC} is the excitation level in open-circuit conditions. With this aim, the generation-recombination balance equation was solved taking into account six recombination mechanisms in silicon, including Shockley–Reed–Hall recombination, radiative recombination, interband Auger recombination, surface recombination, non-radiative exciton recombination, and recombination in the space charge region. The latter two recombination terms are not taken into account in studies of the key parameters of silicon solar cells and in programs for simulating the characteristics of these solar cells. Therefore, in this work their correct definition was performed, their contribution was compared with the contribution of other recombination mechanisms, and it has been shown that the description of the characteristics and key parameters of silicon SC without taking them into account is insufficiently correct. The experimental dependences $\Delta E_g(\Delta n_{OC})$ obtained in the work were compared with Schenk's theory. It has been shown that there is a good agreement between them.

Keywords: silicon solar cell, recombination mechanisms, Schenk's theory.

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1. Introduction

For semiconductors, an important parameter is the concentration of intrinsic charge carriers $n_i(T)$, which significantly depends on temperature T. The concentration of intrinsic charge carriers $n_i(T)$ is a fundamental quantity in semiconductor physics. It is included in almost all calculations related to the injection of charge carriers. The value $n_i(T)$ largely shapes the density of minority charge carriers and significantly affects the recombination properties of semiconductors. Therefore, an accurate determination of $n_i(T)$ is of primary importance both for better understanding of physics and for the design of semiconductor devices.

Diode and transistor semiconductor structures, as well as solar cells (SC) have heavily doped regions with electron and hole conductivity in their composition. In these regions, there is significant narrowing of the width of the band gap of semiconductor ΔE_a (of the order of tens or hundreds meV), related, in particular, to the correlation and exchange interaction of charge carriers, which affects the value $n_i(T)$. There are several models for calculating the effect of band narrowing, both empirical and analytical, and quite a large number of works related to their experimental verification.

Among the theoretical works, one of the most famous is Schenk's model [1]. It is a quantum mechanical calculation at a finite temperature with account of

a number of effects, in particular, the correlation and exchange interaction of charge carriers, in the random phase approximation. It should be noted that although the band-narrowing effect is primarily manifested in heavily doped regions, it also exists in weakly doped regions, primarily due to bipolar injection in diode structures or illumination from the intrinsic absorption band.

In this case, the effect of band narrowing is manifested due to appearance of a sufficiently large concentration of excess electron pairs Δn, the so-called strong excitation level. Although in this case the typical values ΔE_g are of the order of several meV, but even these values of band narrowing in silicon significantly affect the magnitude of the intrinsic concentration of charge carriers and must be taken into account.

For the case of strong doping or excitation, there are many experimental works in which the band-narrowing effect is measured and compared with different theories. Experimentally, in this case, as a rule, the optical properties of silicon are investigated. Most of these works were performed for doping or excitation levels higher than 10^{17} cm^{-3}. Green's work [2] summarizes the results of works in which the experiment was performed within the interval of lower values of doping or injection levels, from 10^{14} to 10^{17} cm^{-3}.

But the optical characteristics of silicon were also measured in these works. This paper offers an approach that allows experimental determining the magnitude of the band-narrowing effect that appears due to illumination or bipolar injection in weakly doped regions. In this case, the current (dark or short-circuit current) is experimentally measured.

The obtained results were compared with Schenk's theory [1]. It was ascertained that there is a sufficiently good correlation between the experiment and the theory. For a better agreement between them, it is desirable to obtain experimental characteristics with greater accuracy, as well as to ensure good thermal stabilization of the studied structures during measurements, since, as noted, the intrinsic concentration strongly depends on temperature.

2. Experimental results on the study of the band-narrowing effect and basic expressions for finding values of the band-narrowing effect in silicon

In the works and programs devoted to modeling the parameters of solar cells, the effect of band narrowing calculated using the Schenk model [1] is taken into account. In [1], when writing the obtained expressions, the notations n_e and n_h are used, which correspond to the full values of concentrations inherent to electrons and holes in the volume of semiconductor.

Let's rewrite them as follows: $n_e = n_0 + \Delta n$, $n_h = p_0 + \Delta n$, where n_0 and p_0 are the equilibrium concentrations of electrons and holes in semiconductor, and Δn is the excess concentration of electron-hole pairs that occurs due to injection or illumination with light from the intrinsic absorption band. At sufficiently high temperatures T, on the order of room temperature, in doped silicon we have $n_0 \cong N_d$ in semiconductor with electron conduction and $p_0 \cong N_a$ in semiconductor with hole conduction. Here, N_d and N_a are the concentrations of shallow donors and acceptors.

Almost all works devoted to the study of the band narrowing effect, with some exceptions, describe the results of the dependence of the value ΔE_g on the level of doping. Much less attention is devoted to the study of its value from the excitation level Δn. So, for example, in the work by Altermatt and Schenk [3], Fig. 1 shows dark *I–V* characteristics for silicon SC only up to applied voltage values not exceeding 0.65 V. And Fig. 2 shows the dependence of the concentration of intrinsic charge carriers only on the level of doping. This is correct only under the condition when Δn is less than n_0, that is, at sufficiently low values of the applied voltage.

At the same time, at the values of the applied voltage higher than those given in [3], the excitation level becomes higher than the doping one, and the value of the intrinsic concentration of charge carriers will also depend on the value Δn. *I.e.*, if you do not limit the value of applied voltage, then the effect of band narrowing and, accordingly, the effective concentrations of intrinsic charge carriers will depend on both the doping level and the excitation one.

Next, we will set the problem of determining the value ΔE_g depending on the level of excitation. For this aim, it is convenient to use the dependence of the short-circuit current density of SC $J_L(I)$ on the open-circuit voltage $V_{OC}(I)$ at various values of the illumination level I. According to the work [4], the open-circuit voltage is found from the expression

$$V_{OC} = \frac{kT}{q}\ln\left(1+\frac{\Delta n_{OC}\left(n_0+\Delta n_{OC}\right)}{n_i(T)^2\exp\left(\Delta E_g(\Delta n_{OC})/kT\right)}\right), \qquad (1)$$

where k is the Boltzmann constant, T – absolute temperature, q – elementary charge, Δn_{OC} – excitation level under open-circuit conditions, $\Delta E_g(\Delta n_{OC})$ – reduction of the band gap dependent on Δn_{OC}, *i.e.*, on the band-narrowing effect, and $n_i(T)$ is the concentration of intrinsic charge carrier [3].

The following expression for the dependence of $\Delta E_g(\Delta n_{OC})$ can be obtained from the formula (1):

$$\Delta E_g\left(\Delta n_{OC}\right) = kT\ln\left[\frac{\Delta n_{OC}\left(J_I\right)\left(n_0+\Delta n_{OC}\left(J_I\right)\right)}{n_i\left(T\right)^2\left(\exp\left(\frac{qV_{OC}\left(J_I\right)}{kT}\right)-1\right)}\right]. \qquad (2)$$

Here, $J_I \equiv J_L\left(J_I\right)$.

The dependence $\Delta n_{OC}(J_I)$ in the case of high-efficient silicon SC can be found from the equation for the generation-recombination balance in the form

$$J_I/q = \left[\frac{d}{\tau_{eff}\left(\Delta n_{OC}\right)}\right]\Delta n_{OC}, \qquad (3)$$

where d is the SC thickness, and $\tau_{eff}(\Delta n_{OC})$ is the effective lifetime of non-equilibrium charge carriers in silicon, which was determined in [5] with taking into account such recombination mechanisms as Shockley–Reed–Hall recombination with the lifetime τ_{SRH}, non-radiative exciton recombination according to the Auger mechanism with participation of a deep impurity level with the lifetime τ_{nr} [6], surface recombination occurring at the front and back surfaces of SC with recombination rates S_0 and S_d, radiative recombination τ_r [7], interband Auger recombination [8] and recombination in space charge region (SCR) with the time τ_{SCR}.

It should be noted that in the works devoted to modeling the characteristics of high-efficient silicon solar cells, such recombination mechanisms as recombination in SCR and non-radiative exciton recombination by the Auger mechanism with participation of a deep impurity level are not taken into account. However, they can play a significant role along with other recombination mechanisms and therefore should be taken into account. Since they take part in formation of the value Δn_{OC}, it is necessary first to justify their importance in determining the dependence $\Delta n_{OC}(J_I)$.

Let's start with recombination in SCR.

3. Recombination in the space charge region

In this work, to calculate the recombination rate in SCR, an approach modified in comparison with our previous works for finding this rate was used. The value of the recombination rate in SCR S_{sc} was calculated using the expression

$$S_{sc}(\Delta n)=\int_0^w \frac{(n_0+\Delta n)dx}{\left[\left((n_0+\Delta n)e^{y(x)}+n_i(T)\exp\left(\frac{E_t}{kT}\right)\right)+b_r\left((p_0+\Delta n)e^{-y(x)}+n_i(T)\exp\left(-\frac{E_t}{kT}\right)\right)\right]\tau_R(x)}. \quad (4)$$

Here, $C_n=V_{nT}\sigma_n$, $C_p=V_{pT}\sigma_p$ are the coefficients, and σ_n and σ_p – capture cross-sections of electrons and holes by the deep level, V_{nT} and V_{pT} – average thermal velocities of electrons and holes, $b_r=C_p/C_n$, $\tau_R=(C_pN_t^*)^{-1}$ – lifetime in SCR, N_t^* – concentration of the deep level in SCR, p_0 – equilibrium volume concentration of holes, $y(x)$ – dimensionless electrostatic potential (band bending) in SCR, E_t – energy of the deep level in silicon SCR, calculated from the middle of the band gap, and w – thickness of SCR.

In the case when $\tau_R=\text{const}$, passing from the integration over the x coordinate to the integration over the dimensionless potential $y=\frac{q\varphi}{kT}$, we obtain

$$S_{sc}(\Delta n)=\int_{y_w}^{y_0} \frac{(n_0+\Delta n)dy}{\left[\left((n_0+\Delta n)e^{y}+n_i(T)\exp\left(\frac{E_t}{kT}\right)\right)+b_r\left((p_0+\Delta n)e^{-y}+n_i(T)\exp\left(-\frac{E_t}{kT}\right)\right)\right]\tau_R}F, \quad (5)$$

where

$$F=\frac{L_D}{\left[(1+\Delta n/n_0)\left(e^{y}-1\right)+y_m+\left(\frac{p_0}{n_0}+\Delta n/n_0\right)\left(e^{-y}-1\right)\right]^{1/2}}. \quad (6)$$

Here, $L_D=\left(\varepsilon_0\varepsilon_{Si}kT/2q^2n_0\right)^{1/2}$ is the Debye length, q – elementary charge, y_0 – is the non-equilibrium dimensionless bending of bands at the surface of the weakly doped area, which depends on the excitation level Δn and is found from the equation of integral neutrality, y_w is the non-equilibrium dimensionless potential at the boundary of SCR near the quasi-neutral area.

To find the dependence of the non-equilibrium dimensionless potential y on the coordinate x, it is necessary to use the solution of the Poisson equation (the second integral) that has the following form

$$x=\int_{y_0}^{y}\frac{L_D}{\left[\left(1+\frac{\Delta n}{n_0}\right)\left(e^{y_1}-1\right)-y_1+\frac{\Delta n}{n_0}\left(e^{-y_1}-1\right)\right]^{0.5}}dy_1. \quad (7)$$

The value of the non-equilibrium dimensionless potential y_0 at $x=0$ is found from the solution of the integral electroneutrality equation that has the form

$$N=\pm\left(\frac{2kT\varepsilon_0\varepsilon_{Si}}{q^2}\right)^{1/2}\left[\begin{matrix}(n_0+\Delta n)\left(e^{y_0}-1\right)-\\-n_0y_0+\Delta n\left(e^{-y_0}-1\right)\end{matrix}\right]^{1/2}, \quad (8)$$

where qN is the surface charge density of acceptors in the p-n junction or in anisotypic heterojunction.

When calculating the recombination rate in SCR, it was assumed that the recombination level responsible for recombination is located near the middle of the band gap ($E_t\approx 0$). In this case, the second terms in square brackets in the denominator (5) can be neglected.

The results of calculating the dependences of the recombination rate in SCR according to the above formulas coincide with the results obtained in the dissertation [9].

In the case when the layer thickness with the lifetime τ_R coincides with the SCR thickness at a very low level of excitation Δn $w(\Delta n\approx 0)$, as the value Δn increases due to the decrease of the value w, part of it

becomes quasi-neutral and recombination according to the Shockley–Reed–Hall mechanism with the lifetime τ_R occurs in it. In this case, the total recombination rate in SCR and the recombination rate in the resulting quasi-neutral area should be taken as the effective recombination rate in SCR.

Its value is equal to

$$S_{SCr} = S_{SC} + \left(\frac{w(\Delta n \approx 0) - w(\Delta n)}{\tau_R}\right)\left(1 + \frac{b_r \Delta n}{n_0 + \Delta n}\right)^{-1}. \quad (9)$$

Fig. 1a shows the theoretical dependences $S_{SC}(\Delta n)$ and $S_{SCr}(\Delta n)$. The parameter of the theoretical dependences is the value of the ratio of the hole capture cross-section to the electron capture cross-section with the recombination center b_r. It was assumed equal to 0.1, 1 and 10. As can be seen from the figure, the smaller the values b_r, the larger the values S_{SC} and S_{SCr}. The figure also shows that in the region $\Delta n > 10^{15}$ cm^{-3} the S_{SCr} values decrease slowly and eventually saturate.

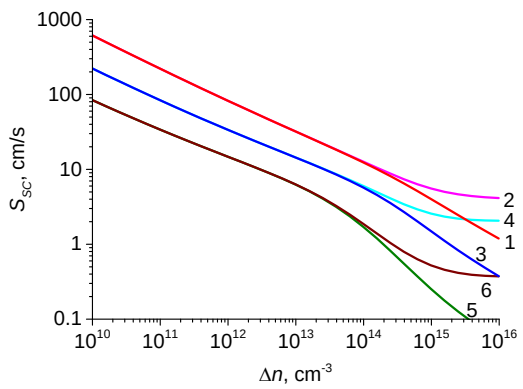

Fig. 1a. Theoretical dependences $S_{SC}(\Delta n)$ (*1*, *3*, *5*) and $S_{SCr}(\Delta n)$ (*2*, *4*, *6*). The used parameters: $\tau_R = 10^{-5}$ s, $n_0 = 10^{15}$ cm^{-3}, b_r = 0.1 (*1*, *2*), b_r = 1 (*3*, *4*), b_r = 10 (*5*, *6*).

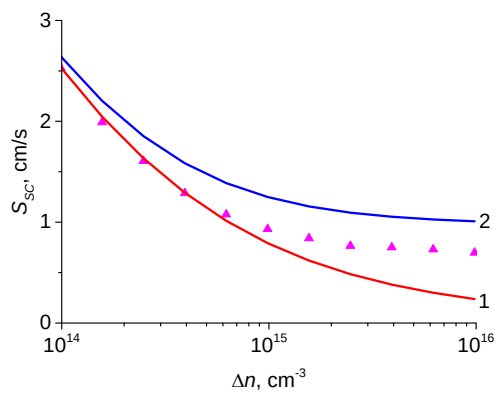

Fig. 1b. Lines – theoretical dependences $S_{SC}(\Delta n)$ (*1*) and $S_{SCr}(\Delta n)$ (*2*) built using the parameters of silicon SC with the record-breaking photoconversion efficiency described in [10]. Triangles –experimental curve [11].

Fig. 1b shows the theoretical dependences of S_{SC} and S_{SCr}, constructed using the parameters of silicon SC with the record-breaking photoconversion efficiency described in [10]. The same figure shows the experimental dependence of the effective recombination rate on Δn for this SC, as well as the theoretical dependence agreed with it and obtained earlier in [11]. When obtaining the latter, it was assumed that the inverse lifetime in SCR is described by Gaussian $\tau_R^{-1}(x) = \tau_m^{-1} \exp\left(\frac{-(x - x_m)^2}{2\sigma^2}\right)$, where τ_m is the lifetime at the maximum point, x_m is the position of the maximum, and σ is the dispersion.

In the work [11], the dependences were constructed using the Gaussian at the following parameter values: $\tau_m = 1.4 \cdot 10^{-5}$ s, $x_m = 2.5 \cdot 10^{-5}$ cm, $\sigma = 4.5 \cdot 10^{-6}$ cm, $b_r = 0.1$. As can be seen from Fig. 1b, the theoretical dependence $S_{SCr}(\Delta n)$ constructed in [11] matches well with the experimental one shown in Fig. 1b. The experimental dependence of the effective recombination rate in SCR in the work [11] was determined as follows. The contribution related with all other recombination mechanisms was subtracted from the total effective lifetime of charge carriers in the bulk determined in the work.

The above examples demonstrate the complexity of the recombination processes in SCR of silicon high-efficient SC, which must be taken into account when considering it.

And in general, as our previous works showed, without taking into account the recombination in SCR, a sufficiently accurate agreement of the experimental characteristics of high-efficiency silicon SC with the theory cannot be obtained. This applies, in particular, to calculations of dependences $V_{OC}(J_I)$, $\Delta E_g(J_I)$ and $\Delta n_{OC}(J_I)$. It is especially important to take into account the recombination in SCR in the area of small and medium excitation levels.

4. Non-radiative exciton recombination by the Auger mechanism with participation of a deep level

Next, we proceed to justify the importance of taking into account the mechanism of non-radiative exciton recombination by the Auger mechanism with the participation of a deep impurity level.

A large number of works are devoted to the study of the influence of radiative recombination and interband Auger recombination in silicon on the bulk lifetime in silicon. Sufficiently complete results of the analysis of the indicated problem are given in the work by Richter and co-authors [8]. In the same work, numerous bibliography on this topic is given. However, despite the fact that at doping and excitation levels greater than 10^{16} cm^{-3}, good agreement between the experimental results and theory is achieved, in our opinion, until recently, it remains unclear what happens in the area 10^{15} cm$^{-3} \le n \le 10^{16}$ cm^{-3} (here, $n = n_0 + \Delta n$).

Thus, in the monograph [12] it was noted that in this area, an additional recombination mechanism related with the introduction of uncontrolled impurities operates. In Fossum's work [13], with references to experimental results in silicon of *n*- and *p*-type conductivity, it was noted that there is an additional recombination mechanism that leads to a decrease in the bulk lifetime $\tau_v(n)$ in silicon, and the law of this decrease is described by an empirical dependence

$$\tau_v(n) = \frac{\tau_{\max}}{1+\dfrac{n}{n_x}}, \quad (10)$$

where $n_x = 7.1\cdot 10^{15}$ cm^{-3}. At the same time, it is said that the value n_x is the same for *n*- and *p*-type semiconductors.

It means that in addition to the Shockley–Reed–Hall recombination mechanism, the non-radiative quadratic recombination mechanism is described by the law as follows

$$\tau_{nr} = \tau_{\mathrm{SRH}}\left(\frac{n_x}{n_0+\Delta n}\right). \quad (11)$$

Finally, the PC1D program and its subsequent versions provide an empirical expression of the form $\tau_v(n) \sim (n/n_x)^{-\alpha}$, which takes into account, as the authors of the program claim, the influence of the material growth technology on the effective lifetime in silicon. The list of the above shows that the matter here is quite complicated. If we are talking about recent works, in particular, the work [8], then such an explanation is not correct, because the authors of this work guarantee that there are no these uncontrolled technological factors.

Below we will show that although the section described by the empirical dependence (10) is absent in a graphical scale in the figures given in the work [8], it is realized with sufficiently careful processing the results of measuring the dependences given in the works [14, 15]. Its presence or absence is defined by the value of the Shockley–Reed–Hall lifetime τ_{SRH}. Even in the case when the value of τ_{SRH} is equal to 30 or 40 ms, such a section is implemented in the dependences shown in Fig. 2 to 4 below (at least in the range of doping or excitation level 10^{15} – 10^{16} cm^{-3}).

Next, it will be shown that the indicated area is determined by the non-radiative recombination of excitons through the recombination channel on a deep impurity, according to the Auger mechanism, considered in the Hangleiter work [15].

4.1. Analysis of literary data by dependences $\tau_{eff}^{v}(n)$

Analyzing the existing works, and first of all the work [6], we will proceed from the fact that the dependence of the effective bulk lifetime $\tau_{eff}^{v}(n)$ in silicon on the doping and excitation levels is described by the following expression

$$\tau_{eff}^{v}(n) = \left[\frac{1}{\tau_{\mathrm{SRH}}(n)}\left(1+\left(\frac{n}{n_x}\right)\right)+\frac{1}{\tau_r(n)}+\frac{1}{\tau_{\mathrm{Auger}}(n)}\right]^{-1}, \quad (12)$$

where $\tau_{eff}^{v}(n)$ is the bulk lifetime in silicon, taking into account both removable and non-removable recombination mechanisms. The removable mechanisms include Shockley–Reed–Hall recombination and quadratic non-radiative recombination τ_{nr}, and the non-removable ones include interband radiative recombination $\tau_r(n)$ and interband Auger recombination $\tau_{\mathrm{Auger}}(n)$.

For the recombination lifetime τ_{SRH} in the case of *n*-type silicon, the expression is used

$$\tau_{\mathrm{SRH}}^{n} \cong \frac{\tau_{p0}(n_0+n_1+\Delta n)+\tau_{n0}(p_1+\Delta n)}{(n_0+\Delta n)}, \quad (13)$$

where $\tau_{p0} = (C_p N_t)^{-1}$s, $\tau_{n0} = (C_n N_t)^{-1}$s, C_p and C_n are coefficients of the hole and electron captures with the recombination center, N_t – concentration, n_1 and p_1 – electron and hole concentrations for cases when the energy position of the recombination level coincides with the Fermi level. For the lifetime of radiative recombination, we will use the relations given in [7].

As for the lifetime of interband recombination $\tau_{\mathrm{Auger}}(n)$, the empirical expression obtained in [8] is used for it.

Before proceeding to the analysis of dependences, we note that the Shockley–Reed–Hall lifetime, depending on the position of the recombination center and the electron and hole capture coefficients, with an increase in the doping and excitation levels, changes between the two positions and can increase, decrease, or remain practically unchanged in a certain range of doping and excitation levels. In what follows, we shall mainly analyze the cases when in the relevant range of doping and excitation levels (from 10^{14} to 10^{17} cm^{-3} for the doping level and from 10^{14} to 10^{16} cm^{-3} for the excitation level), the τ_{SRH} value is constant.

Fig. 2 shows the experimental dependence of the effective bulk lifetime $\tau_{eff}^{v}(n)$ on the doping level in *n*- and *p*-type semiconductors, taken from the work [8], as well as from the works [16–18]. The theoretical dependences $\tau_{eff}^{v}(n)$ were constructed using the expressions (12), (13), as well as dependences (18) and (19) for $\tau_{\mathrm{Auger}}(n)$ taken from the work [8]. For agreement of the theoretical and experimental dependences, in our case, two parameters were varied. One of them is the concentration of the deep centers, which defines the value τ_{SRH}, and the second one is the value n_x. In principle, they can be separated. It requires measurements in the area of doping levels $\leq 10^{14}$ cm^{-3} (at least two points must be measured).

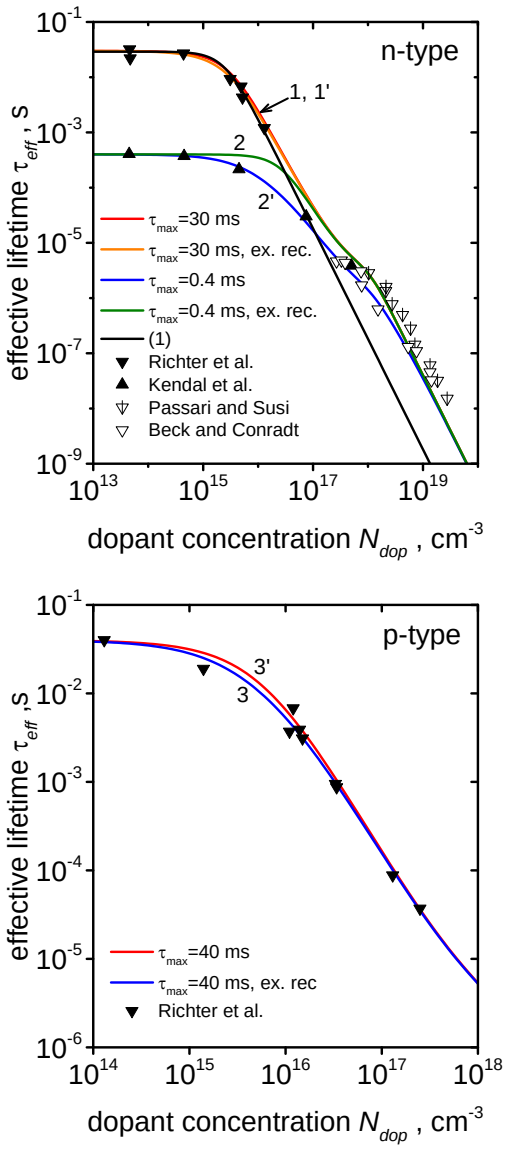

Fig. 2. Experimental dependences of the effective bulk lifetime $\tau_{eff}^{v}(n)$ on the concentration of doping impurity in *n*- and *p*-type silicon. Dots – experiment, lines – theoretical calculation. Curves *1*, *2*, *3* are built with account of exciton non-radiative recombination, curves *1′*, *2′*, *3′* – without it. The used parameters: τ_{SRH}, ms: 30 (*1*), 0.4 (*2*), 40 (*3*); $n_x = 8.2\cdot10^{15}$ cm^{-3}.

Fig. 2a describes the dependences in semiconductor of *n*-type, and Fig. 2b – in *p*-type semiconductor. As can be seen from Fig. 2a, the experimental dependences $\tau_{eff}^{v}(n)$ taken from Richter's work [8], as well as from the works [16–18], agree well with the calculation at $n_x = 8.2\cdot10^{15}$ cm^{-3}. It should be noted that graphic accuracy is not enough to find the value of n_x. Therefore, its value was determined using the method of regression analysis (least squares).

Let's move on considering the dependences for *p*-type semiconductor shown in Fig. 2b. In this case, the calculated curves differ very slightly from the experimental ones both with and without taking into account the additional channel for non-radiative recombination, just like the curve for τ_{max} = 30 ms in Fig. 2a (τ_{max} is actually the value τ_{SRH}).

However, the theoretical dependence $\tau_{eff}^{v}(n)$ taking into account the non-radiative quadratic recombination channel shown in Fig. 2a for the case when τ_{max} = 0.4 ms within the range of doping levels from 10^{15} to 10^{17} cm^{-3} differs significantly from the dependence for which the non-radiative quadratic recombination channel was not taken into account. Experimental points in this case agree with the first dependence. The difference between the two cases, when τ_{max} is large (30 or 40 ms) and small (0.4 ms), becomes clear, if the dependences are plotted in both figures.

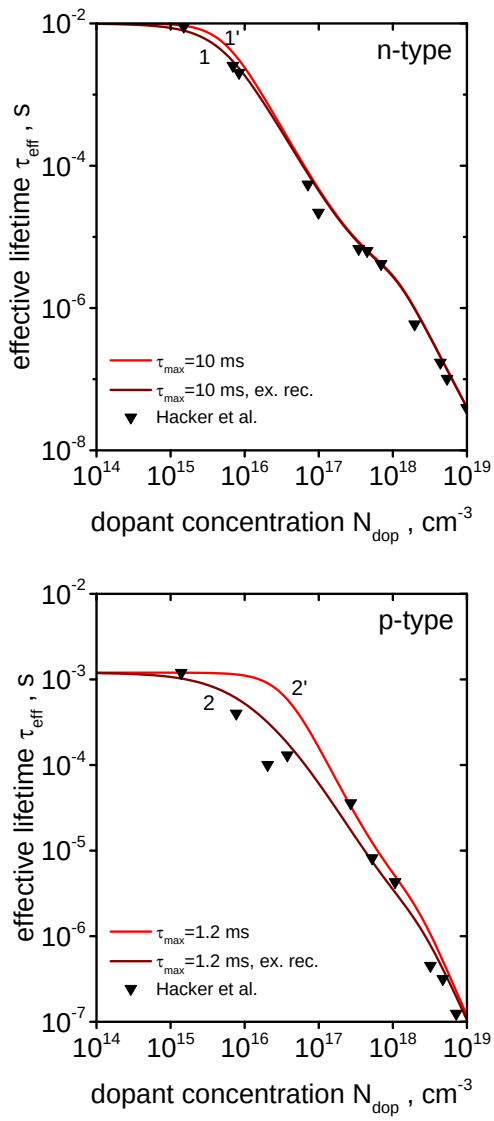

Fig. 3. Dependences of the effective bulk lifetime $\tau_{eff}^{v}(n)$ on the doping level in *n*- and *p*-type silicon. Points – experiment, lines – theoretical calculation. Curves *1*, *2* are built with taking exciton non-radiative recombination into account, curves *1′*, *2′* – without it. The used parameters: τ_{SRH}, ms: 10 (*1*), 1.2 (*2*); $n_x = 8.2\cdot10^{15}$ cm^{-3}.

As can be seen from Figs 2a and 2b, for the case of large τ_{max}, the dependences $\tau_{nr}(n)$ calculated using the formula (11) are much higher than $\tau_{eff}^{v}(n)$. Therefore, they practically (with graphic accuracy) have almost no effect on $\tau_{eff}^{v}(n)$. At the same time, in the case when τ_{max} = 0.4 ms, within the range of doping levels from 10^{16} to 10^{17} cm^{-3}, the dependence $\tau_{nr}(n)$ passes to the left of the dependence constructed without taking non-radiative quadratic recombination into account, and within the range of doping levels from 10^{15} to 10^{17} cm^{-3}, the dependence $\tau_{nr}(n)$ has a rather strong influence on the dependence $\tau_{eff}^{v}(n)$.

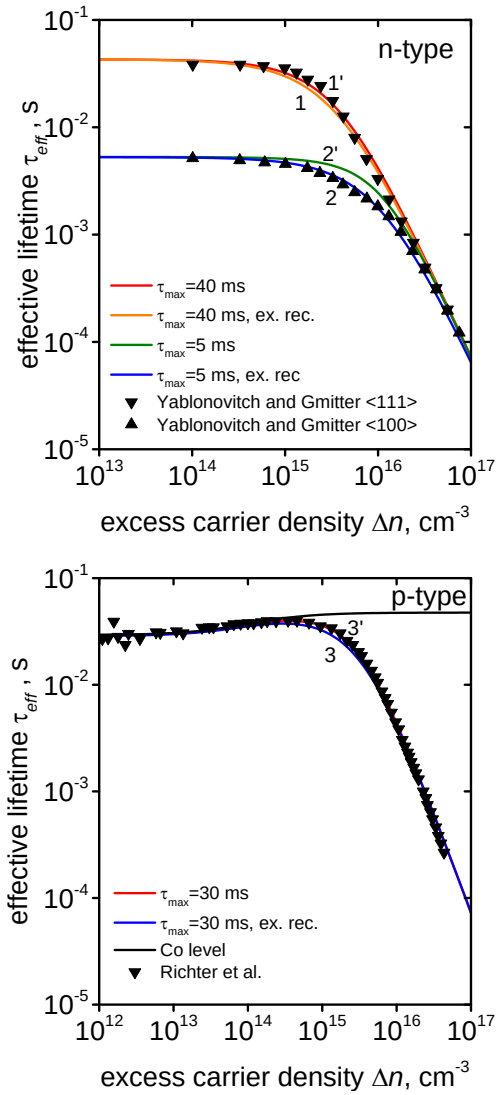

Fig. 4. Dependences of the effective bulk lifetime $\tau_{eff}^{v}(n)$ on the doping level on the excess electron-hole pairs concentration in *n*- and *p*-type silicon. Points – experimental data, lines – theoretical calculation. Curves *1*, *2*, *3* are plotted with account of exciton non-radiative recombination, curves *1′*, *2′*, *3′* – without it. Curve *4* describes the dependence $\tau_{SRH}(\Delta n)$ for the cobalt level. The used parameters: $\tau_{SRH}(\Delta n)$, ms: 40 (*1*), 5 (*2*), 30 (*3*); $n_x = 8.2\cdot10^{15}$ cm^{-3}.

In Fig. 3, the experimental dependences $\tau_{eff}^{v}(n)$ obtained in the work by Hecker and Hangleiter [19] are built. Their comparison with the theoretical dependences $\tau_{eff}^{v}(n)$ with and without account of the non-radiative recombination channel gives a small difference for the case of *n*-type semiconductor and a much larger one for *p*-type semiconductor. The reason is that the value τ_{SRH} for *n*-type semiconductor is 30 ms, and for *p*-type one – 1.2 ms. In this case, the value n_x was also found using regression analysis (the method of least squares) and turned out to be equal to $8.2\cdot10^{15}$ cm^{-3}.

Finally, in Fig. 4 the dependences $\tau_{eff}^{v}(\Delta n)$ are plotted. Experimental points were taken from the works [8, 13]. As before, the difference between the dependences $\tau_{eff}(\Delta n)$ constructed with and without taking into account non-radiative quadratic recombination is small, when τ_{SRH} is equal to 30 or 43 ms, and much larger when τ_{SRH} = 5.2 ms. The value n_x equaled to $8.2\cdot10^{15}$ cm^{-3} was found from the experiment by means of regression analysis.

In this case, the experimental curves for *p*-type semiconductor (Fig. 4b) cannot be agreed with the theory without account of the dependence $\tau_{SRH}(n)$. To agree the theory with the experiment, we assumed that in the case of *p*-type semiconductor, the dependence $\tau_{SRH}(n)$ is defined by the cobalt level with the energy 0.38 eV with τ_{p0} and τ_{n0} equal to $3\cdot10^{-2}$ and $2.2\cdot10^{-1}$ s, respectively. At the same time, it was possible to agree well the theory with the experimental data, both with and without account of the additional channel for quadratic recombination.

Thus, as can be seen from Figs 2 to 4, the influence of quadratic non-radiative recombination on the dependences $\tau_{eff}^{v}(n)$ or $\tau_{eff}^{v}(\Delta n)$ is weaker, the larger the value τ_{SRH}. With graphical accuracy, it can be neglected when $\tau_{SRH} \geq 40$ ms. It should be noted that in modern high-efficiency silicon solar cells typical Shockley–Reed–Hall lifetimes are of the order of 10 ms.

In this case, the error in determining the effective bulk lifetime $\tau_{eff}^{v}(n)$ in the area of maximum power selection in AM1.5 conditions equals from 20 to 30%. This is a rather significant error, and therefore it is incorrect to neglect the consideration of the quadratic non-radiative recombination channel when modeling the parameters of high-efficient silicon solar cells.

As can be seen from the above figures, as the Shockley–Reed–Hall lifetime decreases to values of the millisecond order and less, the influence of the quadratic non-radiative recombination channel increases significantly. This is evidenced, in particular, by the results shown in Fig. 2a for the case when τ_{SRH} = 0.4 ms. In this case, there is a sufficiently long region described by the dependence (10), which does not fit into the theory that takes into account only radiative recombination and interband Auger recombination.

Therefore, a physical explanation of dependences $\tau_{eff}^{v}(n)$ should be sought.

This explanation was proposed simultaneously in the work [20]. Therefore, let's proceed to a brief summary of its results.

4.2. Exciton non-radiative recombination in silicon

In the work [20], it was taken into account that when silicon is illuminated with light of sufficient intensity, in addition to excess electron-hole pairs Δn, excitons with the concentration n_{ex} appear, *i.e.*, there are two subsystems – electron-hole and exciton. It is significant that excitons recombine through the exciton channel, both radiatively and non-radiatively. Although their concentration is low as compared to the value Δn, the value of the non-radiative lifetime of excitons τ_{nr} related to the Auger recombination of excitons on deep impurities can be sufficiently smaller than the Shockley–Reed–Hall lifetime τ_{SRH} in a number of cases.

It leads to the fact that excess electron-hole pairs bind into excitons and recombine through the channel of Auger recombination, which occurs with participation of deep levels. This process was considered at the same time by Hangleiter [15], and he showed that both in the recombination of excitons by the Auger mechanism and in the Shockley–Reed–Hall recombination, the same deep level can participate in them. In the work [20], a phenomenological theory was proposed, it related τ_{nr} and τ_{SRH} between themselves. It was based on these positions. First, it was believed that the non-equilibrium concentrations of electron-hole pairs and excitons in silicon are related by the following equation

$$n_{ex} = \frac{(n_0 + \Delta n)\Delta n}{n^*}, \tag{14}$$

where $n^* = \frac{N_c N_v}{N_x} \cdot \exp\left(-\frac{E_x}{kT}\right)$, N_c, N_v and N_x are the effective densities of states in the conduction, valence, and exciton band, respectively, and E_x is the binding energy of the exciton ground state in silicon. The calculation of n^* for silicon parameters at T = 300 K far from the Mott excitonic transition gave the result $8 \cdot 10^{17}$ cm^{-3}.

The second position is related to the fact (see [15]) that in exciton, electron and hole are spatially correlated. It leads to a significant increase in the probability of Auger recombination, in particular, with participation of impurity centers. The degree of spatial correlation of electron and hole in exciton can be estimated, if we enter the value of the characteristic concentration of electron-hole pairs in exciton, n_L, which is equal to $1/\left[(4/3)\pi a_B^3\right]$, where a_B is the Bohr radius of exciton. Substituting the a_B value for silicon equal to 4.2 nm, we get $n_L \approx 3.3 \cdot 10^{18}$ cm^{-3}. This value is sufficiently large for Auger recombination to occur.

Let's accept that

$$\frac{1}{\tau_{nr}} = n_L G N_t, \tag{15}$$

where G is the parameter of Auger recombination with participation of an impurity, and N_t is the concentration of the impurity level.

Let us compare the recombination fluxes related to recombination of electron-hole pairs in accord with the Shockley–Reed–Hall mechanism ($\Delta n/\tau_{SRH}$) and recombination of excitons (n_{ex}/τ_{nr}). Summarizing them and assuming that $\tau_{SRH} \approx (C_t N_t)^{-1}$, taking into account the relations (14) and (15), we obtain the following expression for the recombination flux R_S involving the Shockley–Reed–Hall recombination and non-radiative exciton recombination

$$R_S = \frac{\Delta n}{\tau_{SRH}}\left(1 + \frac{n_0 + \Delta n}{n_x}\right), \tag{16}$$

where $n_x = n^* C_t / n_L G$.

Estimates made in [20] for the case when the deep level is the gold one give a value that is not significantly different from $8.2 \cdot 10^{15}$ cm^{-3}.

Thus, the above summary of the results of the work [20] shows that the experimental dependence $\tau_{eff}^{v}(n)$ is explained, if taking into account the channel of non-radiative exciton recombination according to the Auger mechanism with participation of a deep impurity level. But the main thing is that the non-radiative exciton recombination channel in silicon with the time τ_{nr} is more efficient than the radiative recombination one.

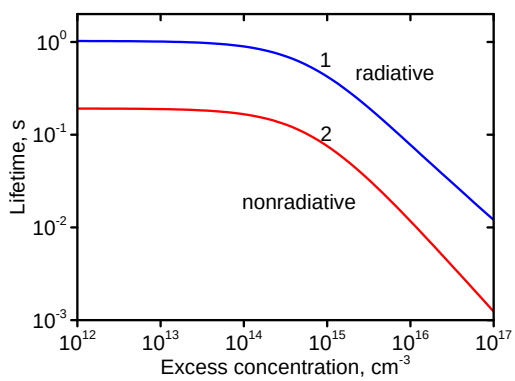

Fig. 5. Theoretical dependences of lifetime of radiative recombination τ_r (1) and non-radiative recombination τ_{nr} (*2*) on Δn for SC described in [10]. The used parameters: τ_{SRH} = 15.2 ms, base thickness – 200 μm, $n_0 = 6.5 \cdot 10^{14}$ cm^{-3}, τ_R = 55 μs, S_0 = 0.0037 cm/s – surface recombination rate at low excitation level, b_r = 0.1, b = 1.8. Here, b is the coefficient in the dependence $EQE(\lambda, b) = \left[1 + \left(4\alpha(\lambda) d n_r^2 / b\right)^{-1}\right]^{-1}$, where EQE – external quantum yield, $\alpha(\lambda)$ – absorption coefficient of silicon depending on the wavelength λ, n_r – refractive index of silicon.

In Fig. 5, the dependences $\tau_{nr}(\Delta n)$ and $\tau_r(\Delta n)$ are plotted for the parameters of the silicon SC, which correspond to the experimental data given in [10]. As can be seen from Fig. 5, the value $\tau_r(\Delta n)$ exceeds the value $\tau_{nr}(\Delta n)$ by more than five times in the whole range of Δn. As the analysis of the corresponding dependences for textured silicon SC shows, the inequality always $\tau_r(\Delta n) > \tau_{nr}(\Delta n)$ holds. Therefore, when considering radiative recombination, it is logical to always take into account non-radiative exciton recombination by the Auger mechanism with participation of a deep impurity level.

5. Finding the experimental value for the case of silicon

Let's move on to the solution of the main problem set in this work, namely, determining the experimental dependences $\Delta E_g(\Delta n_{OC})$. To obtain the experimental dependence $V_{OC}(J_I)$, we used the value $I(V_{OC})$, given in [10] in Fig. 4b. Here, I is the relative intensity of the light flux (the ratio of the light flux to its value at AM1.5). The indicated dependence can be replotted into the dependence $V_{OC}(J_I)$.

To find $\Delta n_{OC}(J_I)$, we used the results of the work [11], in which theoretical modeling of optical and photoelectric characteristics was performed for SC studied in the work [10]. The calculation of the dependence $\Delta n_{OC}(J_I)$ was performed taking into account the effect of band narrowing in the Schenk model.

If the band narrowing is not taken into account in this calculation, then the obtained dependence $V_{OC}(\Delta n_{OC})$ turns out to be unphysical (negative, with a significant amplitude).

Fig. 6 shows the results of calculating the dependence $\Delta E_g(\Delta n_{OC})$ by using the expression (2) and the experimental dependence $V_{OC}(J_I)$ from the work [10].

The doping level of the SC base in this work was $6.5\cdot10^{14}$ cm^{-3}.

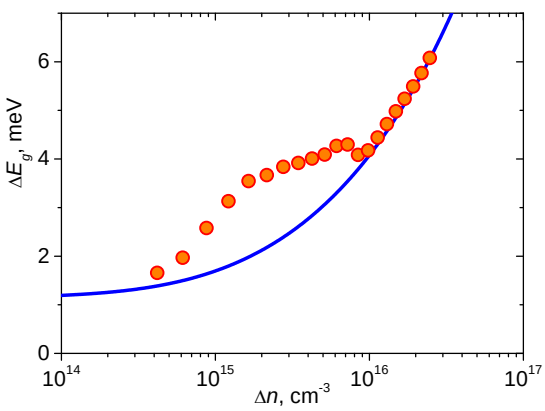

Fig. 6. Experimental (circles) and theoretical dependences $\Delta E_g(\Delta n_{OC})$ (line). The theoretical dependence has been calculated in the Schenk model. Circles were obtained using the experimental dependence $V_{OC}(J_I)$ smoothed using the least-squares method.

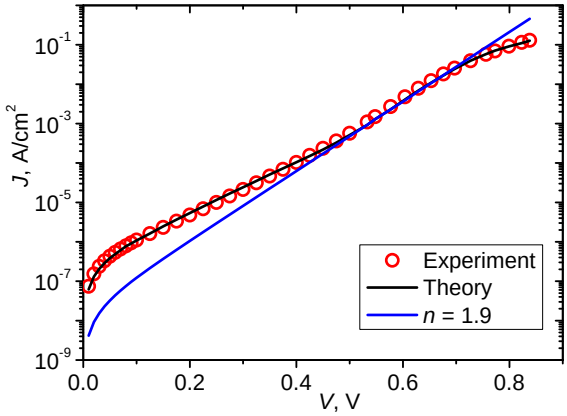

Fig. 7. Dependences of the dark current on the applied voltage obtained in [21], n is a factor of non-ideality.

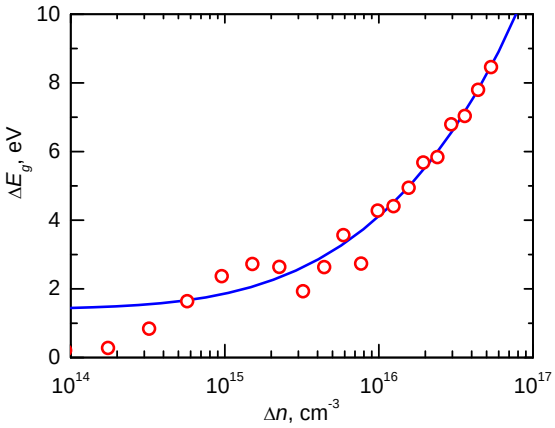

Fig. 8. Experimental (points) and theoretical dependences $\Delta E_g(\Delta n_{OC})$ (line). The theoretical dependence has been calculated in the Schenk model.

The experimental dependence was obtained for the values Δn ranging from $4\cdot10^{14}$ up to $3\cdot10^{16}$ cm^{-3}. The agreement between the experimental data and theory is satisfactory. The maximum deviation of experimental values from theoretical ones in the direction of larger values is about 57%.

Next, we will use to obtain the experimental values $\Delta E_g(\Delta n_{OC})$ of the dependence of the dark current density of silicon SC on the applied voltage $J_T(V)$ obtained in [21] (see Fig. 7). The doping level in this work was 10^{15} cm^{-3}.

Behavior of the dependences $J_T(V)$ differs from that of the dependences $J_I(V_{OC})$ in the first case, because of the series resistance effects on the dark I–V characteristics.

According to [21], the value of the series resistance in this case is 0.65 Ω·cm^2. Having plotted the theoretical dependence $\Delta J = J_T(V, R_s = 0) - J_T(V, 0.65)$ by using the parameters obtained in [21] and adding this value to the experimental value $J_T(V)$, it can be assumed that the obtained dependence is equivalent to the dependence $J_I(V_{OC})$. It was used to find $\Delta E_g(\Delta n_{OC})$. The obtained result is presented in Fig. 8.

As can be seen from the comparison of Figs 6 and 8, in the second case the experimental dependences, with the exception of two points, agree with Schenk's theory even better than in the first case.

This, in our opinion, is probably due to the fact that thermal stabilization in the cryostat, in which the measurements were performed, is better than thermal stabilization using a measuring table in the case of SC from the work [10]. It should be noted, however, that this is primarily true at $\Delta n < 10^{16}$ cm^{-3}, when the influence of series resistance on the dependence is still small, because at higher values Δn the term ΔJ dominates.

To calculate the dependence $\Delta E_g(\Delta n_{OC})$, we also used the dependences $J_I(I)$ and $V_{OC}(I)$ given in [22] for SC based on high-resistance silicon under concentrated illumination, when the maximum illumination power reached almost 100 W/cm^2 (light flux 1000^X AM1.5). The level of doping in this case was $4.43 \cdot 10^{13}$ cm^{-3}. Using the parameters given in the works [22, 23], we calculated the dependences $\Delta n_{OC}(J_I)$, which allowed us to obtain the experimental dependence $\Delta E_g(\Delta n_{OC})$. It is presented in Fig. 9. As can be seen from the figure, the obtained dependence in the region of excitation levels from $9 \cdot 10^{16}$ up to $1.3 \cdot 10^{17}$ cm^{-3} is in good agreement with Schenk's theoretical calculation. As for larger values Δn, as it is known, in the area of lighting powers of ≥ 100 W/cm^2, mechanisms that ensure a decrease in the growth rate of the short-circuit current begin to operate, but they are not taken into account in the theoretical calculation.

In general, the above results indicate that the experimental dependences $\Delta E_g(\Delta n_{OC})$ agree with Schenk's theory. We also note that, unlike the experimental dependences $\Delta E_g(n_0)$ given in many works, we succeeded in obtaining experimental values $\Delta E_g(\Delta n)$ for smaller values Δn.

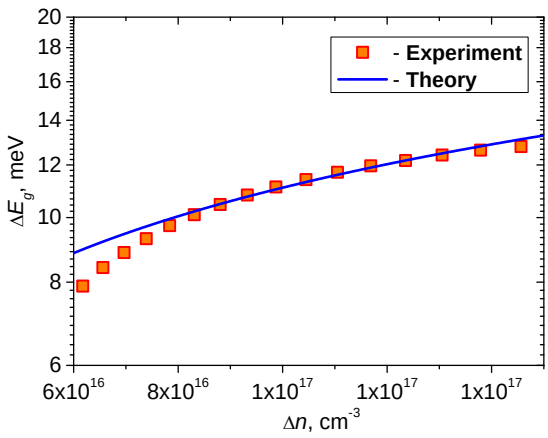

Fig. 9. Experimental (points) and theoretical dependences $\Delta E_g(\Delta n_{OC})$ (line). The theoretical dependence is calculated in the Schenk model.

6. Conclusions

An approach to finding the experimental dependences of the band-narrowing effect on the short-circuit current or light intensity from the intrinsic absorption band in solar cells based on monocrystalline silicon has been proposed. From the solution of the generation-recombination balance equation, the dependence of the short-circuit current density on the excess concentration of electron-hole pairs in the open-circuit mode $J_I(\Delta n_{OC})$ has been obtained.

It enabled to obtain an experimental dependence $\Delta E_g(\Delta n_{OC})$, *i.e.*, the dependence of the value of band-narrowing on the excitation level. The obtained experimental values ΔE_g lie within the range between 2 and 14 meV, which corresponds to the excitation levels from 10^{15} up to 10^{17} cm^{-3}. The obtained experimental values agree with Schenk's theory. These values are significantly smaller than in the case of experimental dependences of the value ΔE_g on the doping level.

The paper also presents results that confirm the legality of using in calculations of effective lifetime for non-equilibrium charge carriers in silicon these components of recombination for recombination current as recombination in the space charge region and non-radiative exciton recombination at a deep volume level with participation of the Auger mechanism (τ_{nr}).

Comparison of theoretical dependences $\tau_{nr}(\Delta n)$ and $\tau_r(\Delta n)$ shows that the value of radiative recombination lifetime $\tau_r(\Delta n)$ within the whole range of Δn is approximately five times greater than that of non-radiative exciton recombination $\tau_{nr}(\Delta n)$, that is, the intensity of recombination along the exciton channel is five times higher than that of radiative recombination.

As these calculations show, the relation $\tau_r(\Delta n) > \tau_{nr}(\Delta n)$ is typical for the case of textured silicon solar cells. It provides an additional basis for using the component of the recombination current $\tau_{nr}(\Delta n)$ in the theoretical modeling of the characteristics of silicon solar cells.

A comparison of the experimental dependences $\Delta E_g(\Delta n_{OC})$ obtained in the work with Schenk's theory has been performed. It has been shown that there is a correlation between them, and in some cases – good agreement. To finally solve the question of the degree of agreement between the indicated values, more accurate measurements of the initial experimental dependences with sufficiently good thermal stabilization of the SC samples are needed.

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Рекомбінація в області просторового заряду, безвипромінювальна екситонна рекомбінація та ефект звуження зон у високоефективних кремнієвих сонячних елементах

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Анотація. Запропоновано вираз для знаходження залежності величини звуження зон у кремнії ΔE_g від рівня освітленості зі смуги власного поглинання I (чи струму короткого замикання). Запропонований вираз застосовано для знаходження експериментальних значень величини ΔE_g у високоефективних кремнієвих сонячних елементах. Залежність $\Delta E_g(I)$ чи залежність $\Delta E_g(J_I)$, де J_I – густина струму короткого замикання, перебудовані в залежність $\Delta E_g(\Delta n_{OC})$, де Δn_{OC} – рівень збудження в умовах розімкненого кола. Для цього було розв'язано рівняння балансу генерації-рекомбінації з урахуванням шести механізмів рекомбінації в кремнії, що включають рекомбінацію Шоклі–Ріда–Холла, випромінювальну рекомбінацію, міжзонну рекомбінацію Оже, поверхневу рекомбінацію, безвипромінювальну екситонну рекомбінацію та рекомбінацію в області просторового заряду. Два останні рекомбінаційні доданки в роботах по дослідженню ключових параметрів кремнієвих сонячних елементів та в програмах по симуляції характеристик цих сонячних елементів до цього часу не враховувались. Тому в роботі виконано їх коректне визначення, проведено порівняння їх внеску з внеском інших рекомбінаційних механізмів та показано, що описання характеристик та ключових параметрів кремнієвих СЕ без їх врахування є недостатньо коректним. Виконано порівняння отриманих у роботі експериментальних залежностей $\Delta E_g(\Delta n_{OC})$ з теорією Шенка. Показано, що між ними існує непогане узгодження.

Ключові слова: кремнієвий сонячний елемент, механізми рекомбінації, теорія Шенка.