

# A novel approach to the surface photovoltage method

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## ABSTRACT

The surface photovoltage technique allows contactless measurement of some electrical parameters of semiconductors. Unfortunately, a contemporaneous approach to steady-state surface photovoltaic (SPV) effect cannot explain the photovoltage spectra, and its application to the determination of the diffusion length is limited to thick samples with thin space charge region (SCR). In this paper a complete theory of steady-state SPV effect is presented that agrees well with the experiment. Consequently, important parameters can be evaluated from the measurements independently of thickness and resistivity of samples. The use of the theory for determining the diffusion length and thickness of the SCR is shown.

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## 1. Introduction

Semiconductor surfaces often display a multitude of states. The charge localized in the states is supplied predominantly by majority carriers from the underlying bulk so that its charge neutrality is consequently disturbed (Fig. 1). The thickness of this space charge region (SCR) is denoted as  $w$ . Concentration of carriers in the semiconductor is usually characterized by potential  $\varphi = (E_F - E_i)/e$  where  $E_F$  is the Fermi level of the semiconductor under study and  $E_i$  is the Fermi level of the intrinsic semiconductor. Potential  $\varphi$  is locally variable and reaches the value  $\varphi_s$  at the surface and  $\varphi_b$  at the bulk. In the non-degenerate case it holds for the concentration at the surface:

$$n_s = n_b \exp[e(\varphi_s - \varphi_b)/kT], \quad p_s = p_b \exp[e(\varphi_b - \varphi_s)/kT] \quad (1)$$

where  $n_b$  and  $p_b$  are concentrations of carriers in the bulk at the boundary with the SCR. Relation (1) is used when solving the Poisson equation, which gives the charge localized in the SCR [1]:

$$Q_{sc} = \frac{\sqrt{2}\varepsilon kT}{eL_D} F\left(\frac{e\varphi_s}{kT}, \frac{n_b}{p_b}\right) \quad (2)$$

where  $L_D$  is the Debye screening length,  $\varepsilon$  is the permittivity of the semiconductor,  $T$  is the absolute temperature,  $k$  is the Boltzmann constant,  $e$  is the charge of electron and  $F$  is the function defined e.g. in Ref. [1].

After illumination the concentrations  $n_b$  and  $p_b$  change to  $n_b^*$  and  $p_b^*$  and the surface potential is  $\varphi_s^*$ . The Fermi level in this non-equilibrium case splits into two quasi-Fermi levels. The surface

photovoltage  $V$  is equal to the change in the band bending after illumination divided by the electron charge. Relations similar to (1) hold if the levels are position independent, which is denoted as the “flat quasi-Fermi level” (FQL) approximation [2].

Electric field in the SCR sweeps the minority carriers from e–h pairs diffusing from the bulk. The charge  $Q_{sc}$  changes to [3]

$$Q_{sc}^* = \frac{\sqrt{2}\varepsilon kT}{eL_D} F\left(\frac{e\varphi_s^*}{kT}, \frac{n_b^*}{p_b^*}, \Delta n\right) \quad (3)$$

$\Delta n$  is concentration of the minority carriers injected into the SCR from the bulk. To find  $\Delta n$ , diffusion equation in the bulk (for  $x > w$ ) must be solved

$$\frac{d^2 \Delta n}{dx^2} - \frac{\Delta n}{L^2} = -\frac{\alpha I \exp(-\alpha x)}{D} \exp(-\alpha x) \quad (4)$$

Here  $I$  is the photon flux density entering at  $x = 0$  into the sample of thickness  $d$ ,  $w$  is the thickness of the SCR,  $\alpha$  is the absorption coefficient,  $L$  is the diffusion length of minority carriers and  $D$  is their diffusion coefficient. For thick bulk ( $\alpha d \gg 1$ ,  $d \gg L$ ) only one boundary condition is needed. Moss [4] in 1955 introduced it in the form

$$D \frac{d\Delta n}{dx} \Big|_{x=w} = s\Delta n(w) \quad (5)$$

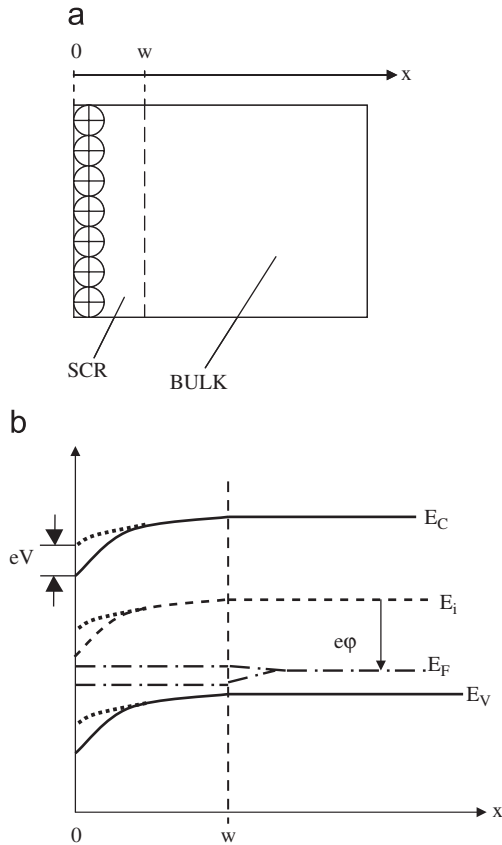
Eqs. (4) and (5) yield the concentration  $\Delta n$  at the SCR–bulk boundary:

$$\Delta n(w) = I \exp(-\alpha w) \frac{\alpha L}{1 + \alpha L s + D/L} \quad (6)$$

Goodman [5] assumed that the photogenerated voltage  $V$  is unknown but monotonic (single valued) function of  $\Delta n(w)$ .

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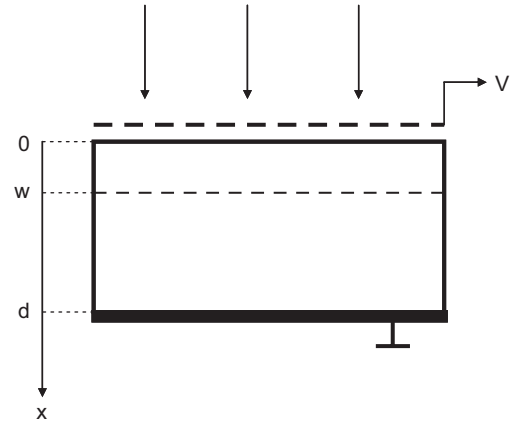
**Fig. 1.** Surface photovoltaic effect in a p-type semiconductor. (a) Localization of majority carriers in traps at the surface. (b) The band diagram of the semiconductor surface. After illumination, the band bending decreases and the Fermi level splits into two quasi-Fermi levels.

Measurement that maintains the surface photovoltaic (SPV) constant implies a constant  $\Delta n(w)$  and, consequently, the right-hand side of Eq. (6) is constant for all  $\alpha$  studied. Neglecting absorption in the SCR ( $\alpha w \ll 1$ ), expression (6) for any wavelength  $\lambda$  can be rearranged to the form [5]

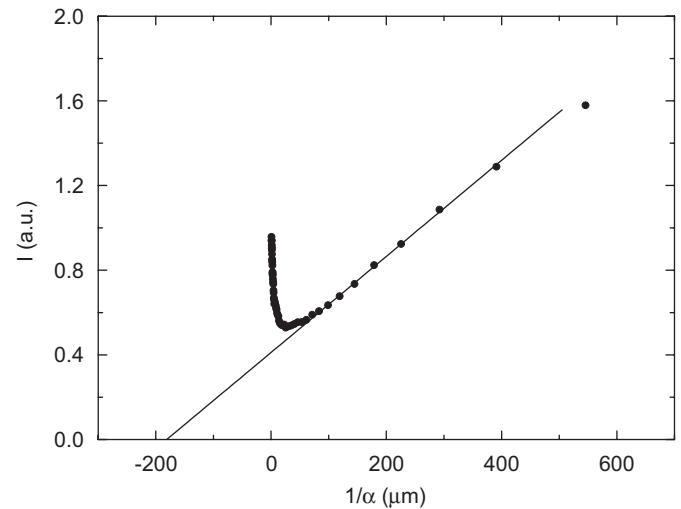
$$I(\lambda) = \text{const}(1/\alpha(\lambda) + L) \quad (7)$$

Assuming  $w \ll L$  Goodman explains the constant  $s$  as the surface recombination velocity at the illuminated surface. It means that  $s$  characterizes the losses of the bulk current in the SCR. The linear function (7) serves for extraction of  $L$  from the SPV spectra in the case of a thick bulk and a thin SCR. Schematic arrangement of the experiment is shown in Fig. 2. The voltage is measured between a semitransparent conductive top electrode and a bottom ohmic electrode. The impinging light is chopped to obtain an alternating signal. An example of application of Eq. (7) is shown in Fig. 3. The absorption coefficients were taken from Ref. [6]. High intensity  $I$  at large  $\alpha$  means a decrease of the SPV signal causing a deviation from the linear plot. It is an influence of recombination in the SCR that was not included in the model.

According to Eq. (5) the diffusion of minority electrons into the SCR is proportional to  $s$ . On the other hand (see Eq. (6)), the increase in  $s$  decreases the concentration  $\Delta n(w)$  and also decreases the injection. This disproportion leads to doubts about the validity of condition (5). Nevertheless, relation (7) holds. It can be derived in a different more rigorous way as shown in the next section. The SPV theory, comprehensively summarized in paper [7], gives the evidence that calculation of the free carrier concentrations at the surface is extremely difficult and till now it was not satisfactorily solved. Consequently, it is a problem to find an



**Fig. 2.** Schematic arrangement of the SPV experiment.



**Fig. 3.** Experimental dependence of the photon flux density  $I$  needed to keep the voltage on a constant value is plotted against the reciprocal value of the absorption coefficient (points). Theory according to Eq. (7) (full line). Silicon sample with concentration  $10^{16} \text{ cm}^{-3}$  and thickness  $460 \mu\text{m}$  was measured in the arrangement as in Fig. 2.  $L = 181.4 \mu\text{m}$  was found using the linear part of the graph.

analytical expression for the photovoltage. Goodman's treatment avoids this difficulty and allows an evaluation of diffusion length in thick samples with thin SCR, but the theory entirely fails in the case of thin wafers with thickness comparable with the diffusion length. This handicap excludes the application of the SPV diagnostics even for most of the silicon wafers for solar cells. Individual authors [8,9] presented a complete theory of the steady-state SPV technique including generation and recombination in the SCR and losses of carriers at the free surface of the sample. In agreement with Goodman [5], they supposed that the recombination processes also influence the bulk current  $J_b$  injected in the SCR. This would mean that the diffusing photocarriers are exposed to additional losses in the SCR and they would always generate lower SPV signals than photocarriers generated in the SCR. Consequently, the SPV signal at a constant photon flux should increase with absorption of light and saturate at the maximum value, which is often inconsistent with experiment.

## 2. A novel model for SPV

In this section we describe our approach to the SPV effect. Instead of concentrations, it is based on a calculation of

photocurrents in the bulk and in the SCR. Unit area of samples is hereafter considered. This simple theory holds without requirements imposed on the thickness of the bulk and the SCR. It is based on two statements:

*Statement (a): in the steady-state regime of measurement the current from bulk  $J_b$  is not influenced by recombination in the SCR*

Considering that in the steady-state the SCR maintains its charge, the statement can be proved as follows: After illumination SCR sweeps the minority photocarriers generated in the bulk. This injection from the bulk enhances their concentration in the SCR. The minority carriers in an excess equal to the amount of the injected ones cannot recombine with the majority photocarriers because these remain in the bulk. The injected carriers must finally leave the SCR because their localization there would cause change in the SCR's charge. This change would be time unlimited because of unlimited illumination. *Statement (a) means that the currents from the bulk ( $J_b$ ) and from the SCR ( $J_{scr}$ ) are independent and can be added.* In addition, the carriers generated in the layer close to the SCR edge do not suffer from recombination and give the highest signal:

*Statement (b): The carriers photogenerated in the SCR contribute to the current  $J_{scr}$  by a "gain factor  $G$ ", which is the ratio of their drift length and the thickness of the SCR*

Consequently, the current  $J_{scr}$  is proportional to the integral of the generation rate  $g(x)$  over the SCR of thickness  $w$  multiplied by the "gain factor"  $G(x)$ .

$$J_{scr} = e \int_0^w g(x)G(x) dx \quad (8)$$

$g(x) = \alpha \exp(-\alpha x)$  and  $G(x) = (I_n(x) + I_p(x))/w = (\mu_n \tau_n E(x) + \mu_p \tau_p E(x))/w$  characterizes the contribution of each photogenerated carrier to the current  $J_{scr}$ , where  $E(x)$  is the electric field in the SCR, and  $I_n, \mu_n, \tau_n$ , and  $I_p, \mu_p, \tau_p$  are drift length, mobility and carrier lifetime of electrons and holes, respectively. The equation for the gain factor follows from the Shockley–Ramo theorem reviewed in Ref. [10] and  $G(x)$  arranged into the above form can be found in Ref. [11]. In fact, the gain factor  $G(x)$  characterizes recombination in the SCR.

The generated voltage corresponds to voltage from a junction in the open-circuit regime [12]:

$$V = \frac{kT}{e} \ln \left( 1 + \frac{J_{ph}}{J_0} \right) = \frac{kT}{e} \ln \left( 1 + \frac{eJ_{ph}}{J_0} \right) \quad (9)$$

where  $J_{ph} = J_b + J_{scr}$ ,  $J_0$  is the saturated dark current and  $eJ_0/J_0$  characterizes the excitation level. The low excitation level means  $J_{ph}/J_0 \ll 1$  and  $V \propto J_{ph}$ . The quantum efficiency defined as  $J_{ph}/eI$  is, consequently, proportional to  $V$ .

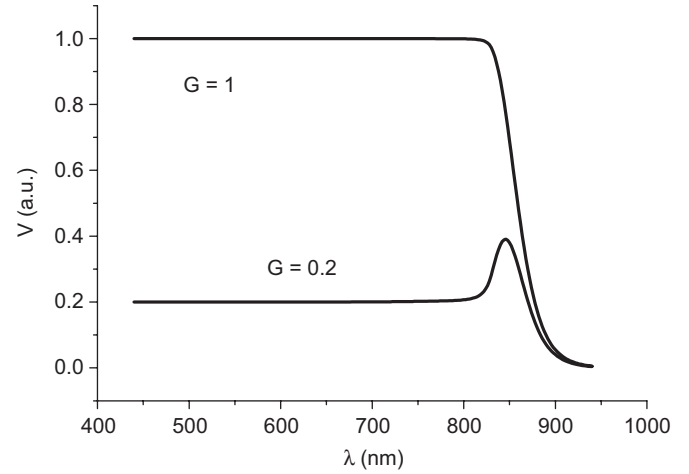
### 2.1. Thick samples

For the sake of simplicity a thick bulk is at first assumed. The photocurrent  $J_b$  entering into SCR from the bulk is diffusion current at  $x = w$ . To find it the diffusion equation (4) for  $\Delta n(x)$  for the case of thick bulk is solved. Assuming that the excess carrier density is reduced to zero by the electric field in the SCR the boundary condition can be defined as  $\Delta n(w) = 0$ , which is fulfilled in most cases.

The bulk current is then easily calculated

$$J_b = eD_n \left. \frac{d\Delta n}{dx} \right|_{x=w} = eI \exp(-\alpha w) \frac{\alpha L}{1 + \alpha L} \quad (10)$$

At this point we show that relation (7) can be derived from Eqs. (9) and (10) for  $\alpha w \sim 0$ ,  $eI/J_0 \ll 1$  and negligible  $J_{scr}$ . Then  $V \propto J_b$



**Fig. 4.** Theoretical SPV spectrum for  $L = 4 \mu\text{m}$  and  $w = 2 \mu\text{m}$ . The gain factor  $G$  is assumed to be a constant. The curves are calculated using absorption coefficients from Ref. [13].

and the relation follows from Eq. (10) if the voltage is maintained constant.

The photocurrent from the SCR is given by relation (8) and the total SPV calculated according to Eq. (9) is shown in Fig. 4 for two values of the gain factor that are assumed to be constant. This figure shows the effect of recombination in SCR on the spectrum. Curve  $G = 1$  characterizes the SPV spectrum without losses in the SCR. High signal in a wide spectral region is caused by the prevailing absorption in the SCR.

Curve  $G = 0.2$  demonstrates recombination in this region. The peak in curve  $G = 0.2$  results from bulk contribution, which prevails over that from the SCR.

### 2.2. Thin samples

If the thickness of the samples is small so that photogenerated carriers also appear at the bottom surface, the sample is assumed to be thin. Hereafter currents generated in the SCRs are neglected. To obtain the bulk currents Eq. (4) should be solved with two boundary conditions (see Fig. 5), namely:

$$\Delta n(w_1) = 0 \text{ and } \Delta n(w_1 + d) = 0 \quad (11)$$

where  $w_1$  is the thickness of the top SCR.

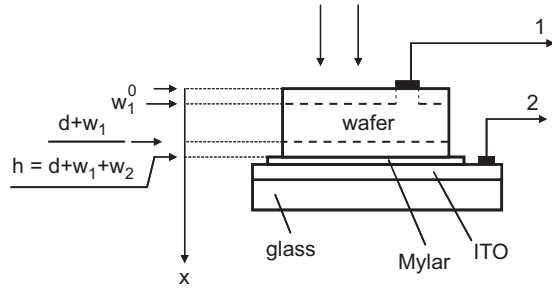
In thin samples multiple reflections from the front surface with reflection coefficient  $R_1$  and the bottom surface with the coefficient  $R_2$  were assumed.

The current  $J_{b1}$  injected into the front SCR is [14]

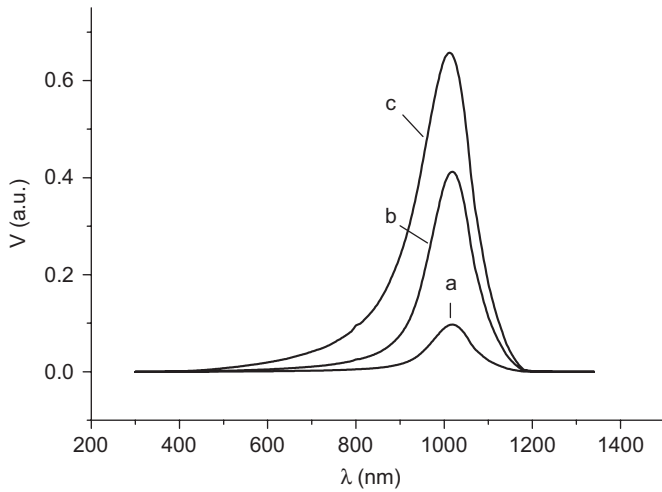
$$\begin{aligned} J_{b1} = eD \left. \frac{d\Delta n}{dx} \right|_{x=w_1} &= a_1 \exp(-\alpha w_1) \frac{\alpha L}{(1 - \alpha^2 L^2)} \\ &\times \{ [\cos h(d/L) - \exp(-\alpha d)] / \sin h(d/L) - \alpha L \} \\ &- a_2 \frac{\alpha L}{(1 - \alpha^2 L^2)} \times \{ [1 - \cos h(d/L) \exp(-\alpha d)] \\ &/ \sin h(d/L) - \alpha L \exp(-\alpha d) \} \end{aligned} \quad (12a)$$

and the current  $J_{b2}$  injected into the bottom SCR is [14]

$$\begin{aligned} J_{b2} = eD \left. \frac{d\Delta n}{dx} \right|_{x=w_1+d} &= a_1 \exp(-\alpha w_1) \frac{\alpha L}{(1 - \alpha^2 L^2)} \\ &\times \{ [\cosh(d/L) - \exp(-\alpha d)] / \sinh(d/L) - \alpha L \} \\ &- a_2 \frac{\alpha L}{(1 - \alpha^2 L^2)} \times \{ [1 - \cosh(d/L) \exp(-\alpha d)] / \sinh(d/L) \\ &- \alpha L \exp(-\alpha d) \} \end{aligned} \quad (12b)$$



**Fig. 5.** The concept of measurements of thin samples. The voltage is taken from the bottom SCR. The bulk is contacted by means of the top electrode 1. The thicknesses of the SCRs are  $w_1$  and  $w_2$ .



**Fig. 6.** Theoretical SPV spectra of thin Si sample in the arrangement as in Fig. 5. The curves are plotted for thickness  $h = 300 \mu\text{m}$ , negligible thicknesses of the SCRs and  $R_1 = R_2 = 0.316$ . Absorption coefficients are taken from [6]. Curve a:  $L = 80 \mu\text{m}$ ,  $el/J_0 = 1$ ; curve b:  $L = 80 \mu\text{m}$ ,  $el/J_0 = 5$ ; curve c:  $L = 200 \mu\text{m}$ ,  $el/J_0 = 5$ .

$$a_1 \equiv el(1 - R_1)/(1 - R_1 R_2 \exp(-2\alpha h))$$

$$a_2 \equiv el(1 - R_1)R_2 \exp(-\alpha h)/(1 - R_1 R_2 \exp(-2\alpha h))$$

The currents  $J_{ph1} = J_{b1}$  and  $J_{ph2} = J_{b2}$  are of opposite sign and the relevant voltages at least partially compensate one another, which complicates the parameter evaluation. An auxiliary electrode contacting the bulk allows the measurement of each voltage separately [15]. Fig. 5 demonstrates the measurement of the SPV generated at the bottom SCR. The shape of the SPV signal depends on the  $el/J_0$  ratio and on the diffusion length. Despite the low intensity of light reaching the bottom SCR–bulk interface quite a high signal can be generated there depending on the value of  $J_0$ . While increasing  $el/J_0$  widens the spectrum (curves a, b in Fig. 6), the diffusion length enhances the signal predominantly at short wavelengths (curve c in Fig. 6). Increasing absorption of light (decreasing wavelength) leads to lower efficiency of carrier collection especially for the carriers generated at a longer distance from the bottom SCR–bulk boundary.

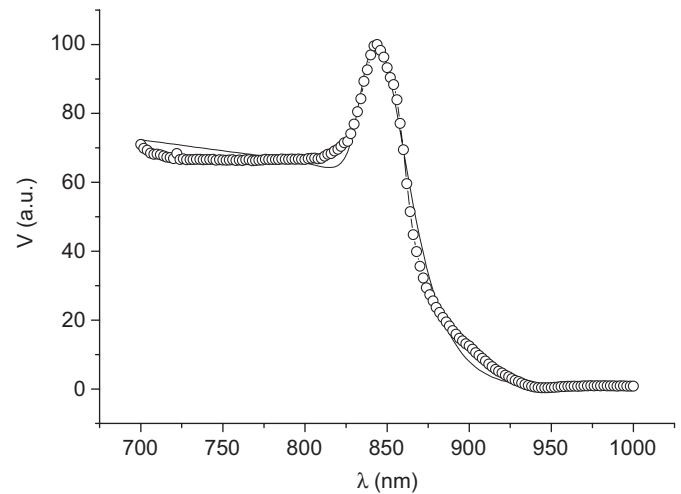
### 3. Experiment

The CdTe samples were evaluated using absorption coefficients from Ref. [13]; absorption coefficients from Ref. [6] were employed for the Si samples. An example of the measurement of a thick CdTe sample in arrangement as in Fig. 2 is shown in Fig. 7. The theoretical curve was calculated according to Eq. (9) where

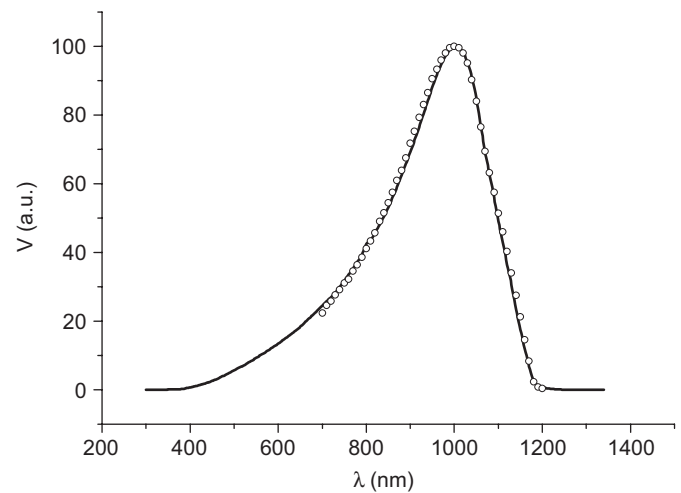
the photogenerated current is the sum of components (8) and (10). Local variability of the gain factor  $G$  is considered [16]. The independence of the two contributions allows us to determine not only the diffusion length but also thickness of the SCR.

The reliability of diffusion length evaluation in thick samples measured in the arrangement according to Fig. 2 depends on the ratio of the diffusion and drift components in the SPV spectrum [17].

As an example of measurement of thin samples Fig. 8 is shown. Negligible contribution of both SCRs characterizes the SPV spectrum of the Si monocrystalline wafer for solar cells. A low value of  $el/J_0$  means that the logarithm in Eq. (9) can be developed so that SPV changes linearly with the intensity of light and, consequently, its normalized spectrum is independent of the light intensity. Only one parameter ( $L$ ) characterizes the SPV spectrum.



**Fig. 7.** Normalized SPV spectrum of compensated tin-doped thick sample CdTe with  $\rho \approx 10^3 \Omega \text{cm}$  measured in the arrangement according to Fig. 2. The theoretical curve (full line) was plotted for the parameters  $L = 2 \mu\text{m}$ ,  $w = 2 \mu\text{m}$  and  $h = 1.5 \text{ mm}$ . The gain factor is locally variable. The SCR strongly influences the spectrum [17].



**Fig. 8.** Normalized SPV spectrum of thin silicon wafer for solar cells measured in the arrangement according to Fig. 5. The theoretical curve (full line) containing contribution from the bulk only was plotted for the parameters  $L = 222 \mu\text{m}$ ,  $d = 250 \mu\text{m}$  and  $el/J_0 = 0.01$ . Excellent fit means that the both SCRs do not influence the spectrum.

#### 4. Conclusion

The conventional model of the SPV cannot sufficiently explain the SPV spectra, and its application is limited to thick samples with thin SCR. Our new conception of surface photovoltage is based on the calculation of the photogenerated currents characterized as follows:

- (1) The photocurrents generated in the bulk and in the SCR are independent and can be added.
- (2) Photocurrent from the SCR can be calculated by introducing a gain factor characterizing the contribution of photocarriers to the current. The gain factor can be locally variable.

The model is verified on “thin” conductive Si samples and “thick” resistive CdTe samples. Arrangement for measurement of “thin” samples takes the voltage at the bottom SCR. This eliminates the contribution from the top SCR to the photocurrent, which facilitates the evaluation of the diffusion length.

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