SIMULATING THE EFFECT OF INHOMOGENEITY OF THE THICKNESS OF NANOCRYSTALLINE TiO_2 LAYERS ON THE DIFFUSION OF CHARGE CARRIERS IN SOLAR CELLS BASED ON A DISPERSION HETEROJUNCTION WITH DYE

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We study the diffusion transport in a nanocrystalline TiO_2 layer of a solar cell with dye for various values of the dispersion of the thickness of a TiO_2 layer. A model of the transport, which considers the influence of the dispersion of the thickness of a TiO_2 layer on the total response of the electrolyte/TiO_2/FTO system under pulse laser irradiation, is developed. In the model, the motion of charge carriers through such a TiO_2 layer is described as a motion through the system of parallel TiO_2 links with various lengths. In the presence of the dispersion of the thickness of a TiO_2 layer described by the Gauss function, the coefficient of diffusion of charge carriers increases and the position of the diffusion peak shifts to shorter times as compared with the dispersionless case. We calculated the dispersion of the coefficient of diffusion for specimens with a distribution over thicknesses measured with a profilometer.

1. Introduction

Recently, solar cells and phototransducers on the basis of dispersion heterojunctions with dyes are strongly studied and designed. A basis of such structures is a mesoporous layer TiO_2, whose pores contain a dye applied to a conductive transparent support FTO (SnO_2 doped with fluorine). Solar cells on their basis promise to be a cheap alternative to traditional Si solar cells of the n–p type. The efficiency of such structures reaches 11% and 8.1%, respectively, for structures with the use of electrolyte and a polymer as a donor conductor [1, 2]. The theoretical calculations indicate the possibility to attain the efficiency up to 33% [1]. The use of a mesoporous material allows one to guarantee the absorption surface of 200–300 m^2/g as compared with 10 m^2/g for plane surfaces [3]. According to [4], the molecules of a dye absorbed on the surface of TiO_2 must ensure the stable operation of a solar cell during 20 years. The principle of the operation of a dye-sensitized solar cell is shown in Fig. 1,*a*. The incident photon is absorbed by a dye positioned on the surface of nanocrystalline TiO_2 particles and causes the transition of an electron from the molecular ground state S^0 to a higher excited level S^*. The excited electron is injected in the conduction band of TiO_2 particles, by leaving, in this case, the dye molecules in the oxidized state S^+. The injected electron diffuses across the system of interconnected TiO_2 nanoparticles to a conductive transparent support (FTO-layer, anode) applied to glass and then to the cathode through the external resistance. The cathode electrode takes participation in the creation of iodine, I^-, from iodide-ion I_3^- in electrolyte. The cycle is closed by the reduction of oxidized molecules of a dye with the help of iodine I^-. The transport properties of such a system depend on a morphology of the TiO_2 layer, properties of the surface, and properties of the electrolyte. In the present work, we simulate the influence of the inhomogeneity of the thickness of a layer TiO_2 on the diffusion of charge carriers across the TiO_2 layer by describing the thickness inhomogeneity with a

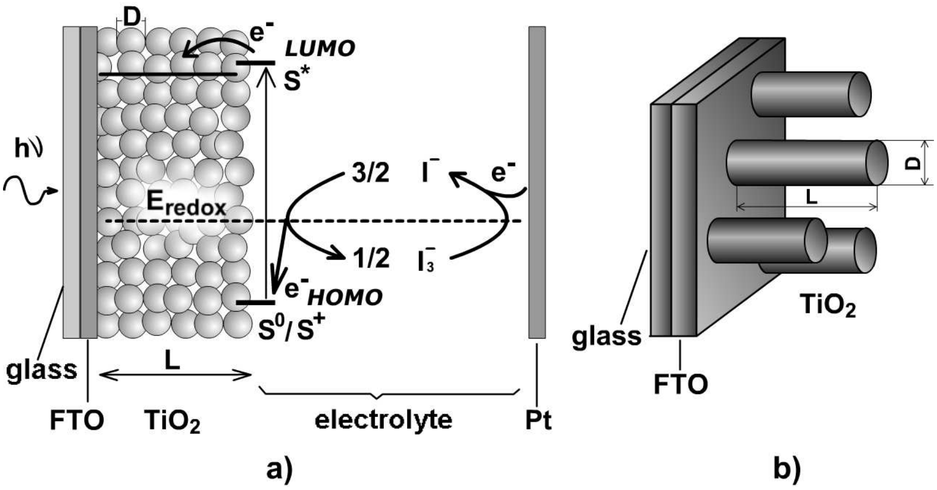

Fig. 1. *a* Scheme of a solar cell with dye; *b* model representation of a TiO_2 layer as the system of TiO_2 cylinders with a variable length and a constant diameter D

Gauss function and the distribution function obtained as a result of measurements of the thickness inhomogeneity of TiO_2 layers with a profilometer.

2. A model of Dispersion Heterojunction

The system of interconnected TiO_2 nanoparticles which form conducting chains (see Fig. 1,*b*) can be presented as a collection of cylinders [5, 6] of length L_i and diameter $D = \text{const}$.

The transport properties of the electrolyte/TiO_2/FTO system are analyzed with the help of transient characteristics, by studying the dependence of a response of the system (the electric current in the external circuit) after the irradiation with a laser pulse with $\lambda = 337$ nm, $\tau_{\text{pulse}} = 5$ ns. In the present work, we consider the influence of the inhomogeneity of the thickness L of a TiO_2 layer on the total photoresponse of the system.

The mesoporous layer TiO_2 of a solar cell can be presented by a model describing a conducting TiO_2 layer as N conducting link-cylinders made of TiO_2 on unit area (see Fig. 1,*b*). In this case, we assume that the distribution of links over lengths can be described by the Gauss function

$$f = \frac{1}{\sigma\sqrt{2\pi}} e^{\frac{-(t-\mu)^2}{2\sigma^2}}. \qquad (1)$$

The parameter μ characterizes the mean thickness of a TiO_2 layer, L_{av}, and the parameter σ describes the dispersion of the thickness of a TiO_2 layer. A response of the system can be described with the help of the equivalent scheme presented in Fig. 2.

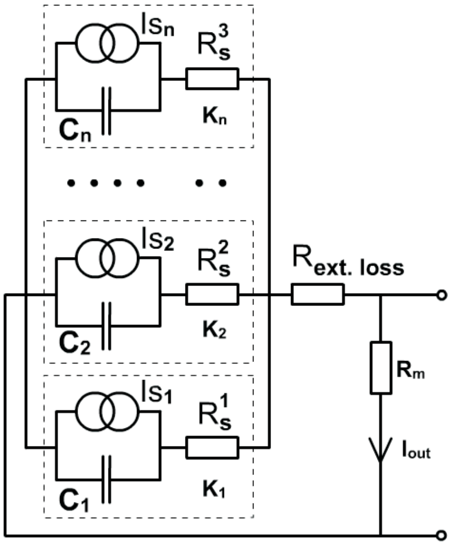

Fig. 2. Equivalent scheme of the electrolyte/TiO_2/FTO system with regard for the inhomogeneity of a TiO_2 layer

Each parallel branch of the equivalent circuit is a separate link (a cylindrical conductor) in the system of TiO_2 links. The generation of carriers is represented by the current source Is_i. The separation of charges is represented by a capacitor C_i. The effect of the series resistance of a TiO_2 link is given by the resistor R_s^i. The other elements are as follows: $R_{\text{ext.loss}}$ takes the losses in the external circuit, and R_m is the measuring resistance.

The resistance of an elementary link R_s^i can be presented as

$$R_s^i = R_{\text{TiO}_2}^i + R_{\text{el}}^i, \qquad (2)$$

where $R^i_{\mathrm{TiO_2}}$ is the resistance of the elementary i-th link of thickness $L^i_{\mathrm{TiO_2}}$, R^i_{el} is the resistance of the layer with electrolyte of thickness L^i_{el} between the interface of TiO$_2$/electrolyte and a Pt-electrode. The distance between the FTO layer and the Pt-electrode is $L_{\mathrm{FTO-Pt}}= L^i_{\mathrm{TiO_2}}+L^i_{\mathrm{el}} = \mathrm{const}$.

But the physical processes running in the system, namely the diffusion and recombination of current carriers through the system of connected TiO$_2$ particles, cannot be modeled by an equivalent scheme which contains only passive elements. We performed the simulation of these physical processes with the use of differential equations and the account of their properties in the active source of current [7].

In order to realize the simulation, the whole range of thicknesses was discretized and represented by 21 values. The number N_i of relevant links of thicknesses $L^i_{\mathrm{TiO_2}}$ was determined by the Gauss distribution. The average thickness of a TiO$_2$ layer was taken 9.1 μm, the specimen area was equal to 0.49 cm^2, and the dispersion of the thickness of a TiO$_2$ layer was described by the parameter σ varying from 0.1 to 3 μm. Since the average thickness $L^{\mathrm{av}}_{\mathrm{TiO_2}}$ of each elementary link-cylinder ($L^{\mathrm{av}}_{\mathrm{TiO_2}}$ is from several to tens of micrometers) is much larger than the diameter of a link-cylinder, $D = 5 \div 50$ nm, and elementary link-cylinders are axisymmetric, it was expedient to pass to the consideration of a one-dimensional structure in order to simplify the simulation. Therefore, we took only the longitudinal component of the coefficient of diffusion into account. For each value of the thickness $L^i_{\mathrm{TiO_2}}$, we solved numerically the nonstationary diffusion equation with regard for the recombination with the corresponding boundary (2b) and initial conditions (2c) and determined the contribution $j_i(t)$ of each separate i-th link to the total response of the system $j_\Sigma(t)$:

$$\frac{\partial n(x,t)}{\partial t} = D\frac{\partial^2 n(x,t)}{\partial x^2} - \frac{n(x,t)}{\tau}, \tag{2a}$$

$$D\frac{\partial n(0,t)}{\partial x} = 0, \tag{2b}$$

$$kn(L^i_{\mathrm{TiO_2}},t) + D\frac{\partial n}{\partial x} = 0,$$

$$n(x,0) = \mathrm{const}\ \exp(-\alpha\, x), \tag{2c}$$

where D the coefficient of diffusion, τ the lifetime of electrons, and k the coefficient of extraction of electrons from the TiO$_2$ layer into the FTO layer.

By using the solutions of the differential equations for all links with regard for the influence of elements of the external circuit, we calculated the total response of the system:

$$j_\Sigma(t) = f(\sum_{i=i}^{H} N_i j_i(t), R_m, R_{\mathrm{ext.loss}}). \tag{3}$$

Solving Eqs. (2a)–(2c) was realized within the software Matlab with the use of the module Partial Differential Equation Toolbox [9]. The simulation of the influence of the external circuit on transient characteristics was carried out with the use of the module Simulink within the software Matlab.

3. Analysis of Results

The results of the simulation are given in Fig. 3. We studied the dependences of the position of the maximum of the diffusion peak t_{peak}, the coefficient of diffusion D_{eff}, and the charge extracted from the TiO$_2$ layer into the external circuit, Q, on the coefficient of dispersion of the thickness. In the simulation, we used the following parameters: $D_{\mathrm{eff}} = 6\times10^{-5}$ cm^2/s, $k = 10$ cm/s, $\tau = 10$ s, R_m=1 MΩ, $R_{\mathrm{ext.loss}} = 5$ Ω, $C_i = 60$ nF/cm^2, $\rho_{\mathrm{el}} = 8$ Ω·cm, $\rho_{\mathrm{TiO_2}} = 0.178$ MΩ·cm. The given values k and τ allow us to study the influence of of the thickness dispersion on a photoresponse.

As seen from Fig. 3*a*, the position of the diffusion peak t_{peak} shifts to the region of shorter times with increase in σ from 0.1 μm to 3 μm, which corresponds to the increase in the effective coefficient of diffusion D_{eff} by a factor of $\sim$1.5. The change of σ does not practically affect the variation of Q.

Under the change of σ in the given limits, Q decreases by a value less than 0.1%.

As seen from Fig. 3,*b*, the range of variation of the coefficient of dispersion of the thickness of a TiO$_2$ layer σ can be conditionally divided into two subranges: those with small ($\sigma = 0.1 \div 1$ μm) and great ($\sigma = 1 \div 3$ μm) variations of t_{peak} and D_{eff}. The dependence of D_{eff} on the coefficient of dispersion σ can be approximately described with the help of the formula $D_{\mathrm{eff}} = D^0_{\mathrm{eff}} + A\exp(R\sigma)$, where $D^0_{\mathrm{eff}} = 5.8\times10^{-5}$ cm^2/s, $A = 1.3498\times10^{-6}$, and $R = 10330$.

Let the distribution of the thickness be described by (1), and let the average thickness of a TiO$_2$ layer be constant. Then the shift of a position of the diffusion peak t_{peak} to the left on the time scale with increase in the inhomogeneity of the thickness of a layer TiO$_2$ is

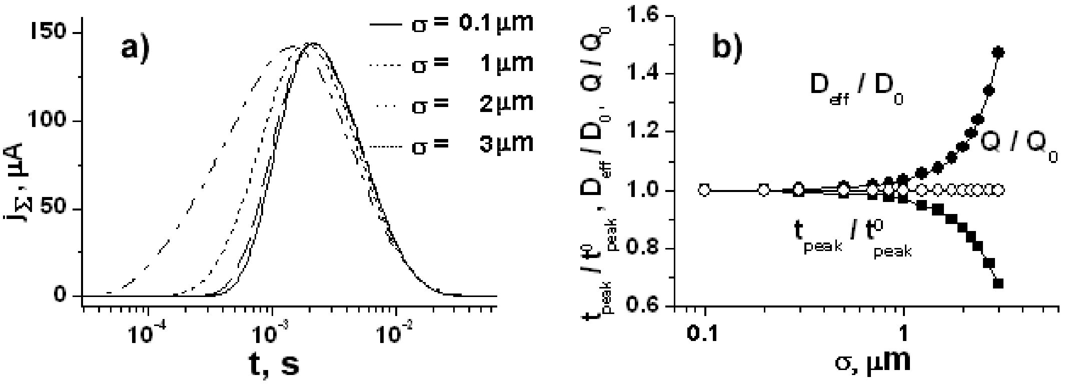

Fig. 3. *a* – Calculated photoresponse of the electrolyte/TiO_2/FTO system for various values of the coefficient of dispersion of the thickness of a TiO_2 layer, σ; *b* – dependence of D_{eff}, the position of the diffusion peak t_{peak}, and charge Q on the coefficient of dispersion of the thickness of a TiO_2 layer, σ

explained by that the diffusion of electrons runs in the TiO_2 layer with effective thickness L_{eff} which is less than the average thickness of the layer L_{av}. The Gauss distribution of TiO_2 links over length gives a symmetric distribution of lengths relative to L_{av}. At the same time, the contribution j^- of a TiO_2 link with length $L^-_{\text{av}} = L_{\text{av}} - \Delta$ to the total response of the whole system is greater than the contribution j^+ of a TiO_2 link with length $L^+_{\text{av}} = L_{\text{av}} + \Delta$. The following condition holds:

$$j^-(t, L_{\text{av}} - \Delta) > j^+(t, L_{\text{av}} + \Delta). \quad (4)$$

This condition is satisfied because the maximum amplitude of the diffusion peak $j^{\max}_{\text{peak}}$ depends nonlinearly on the thickness of a link, along which the diffusion of electrons occurs.

To clarify the influence of the real distributions of inhomogeneous thicknesses of TiO_2 layers on transient characteristics, we studied the TiO_2/FTO structures. The layers of TiO_2 were deposited by electrophoretic spraying [8] with the following annealing for 30 min at a temperature of 450 °C. On the first stage, the solution of nanodimensional TiO_2 particles in an aqueous or organic solvent is formed. In this case, it is possible to control the size of TiO_2 nanoclusters by controlling the processes of hydrolysis and condensation. On the second stage, there occurs the process of electrophoretic deposition of nanoparticles on the electrode. Under the action of the electric field, charged particles move to the collecting electrode. The mobility of particles depends on the dielectric constant of the solution, electrokinetic potential of particles, and viscosity of the solution. Within this method, the maximum package density for homogeneous spherical particles is 74% and can be controlled by the concentration of nanoparticles in the solution, electrokinetic potential, the intensity of an applied electric field, and the kinetic processes running on the surface of particles.

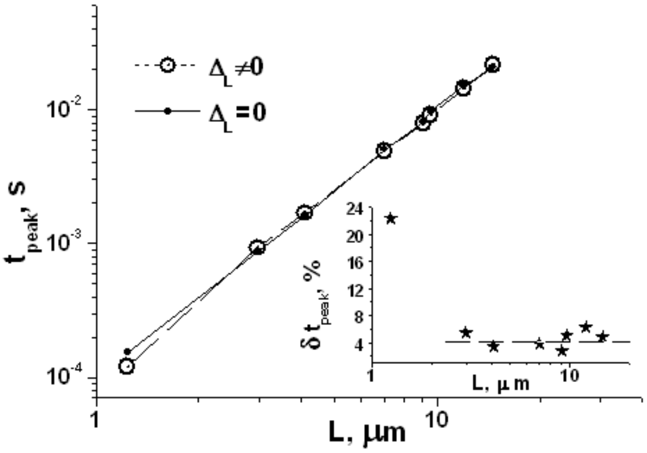

Fig. 4. Dependences of the position of t_{peak} on the thickness of a TiO_2 layer for the homogeneous ($\Delta^i_L = 0$) and inhomogeneous ($\Delta^i_L \neq 0$) distributions of the layer thickness. The insert shows the relative deviation of $t_{\text{peak}}(\Delta^i_L = 0)$ from $t_{\text{peak}}(\Delta^i_L \neq 0)$

In experiments, we studied 8 specimens which had the following average thicknesses L^i_{av}: 1.24, 2.98, 4.1, 7, 9.1, 9.6, 12, 14.6 μm. For each specimen, we measured the thickness $L = f(x)$, where x is the coordinate, of a TiO_2 layer with a profilometer. We calculated the distribution of elementary links over thicknesses, which characterizes the homogeneity of the thickness of a TiO_2 layer, by assuming that the distribution along the y-coordinate is the same as along the x-coordinate.

Each specimen with L^i_{av} was characterized by the own thickness inhomogeneity. We did not observed a monotonic dependence of the parameter of inhomogeneity on the thickness of a TiO_2 layer. In Fig. 4, we present the calculated responses of the system to a laser pulse for a homogeneous TiO_2 layer $L^i = L^i_{\text{av}}(\Delta^i_L = 0)$ and for an inhomogeneous TiO_2 layer $L^i \neq L^i_{\text{av}}(\Delta^i_L \neq 0)$. The nonmonotonic dependence of δt_{peak} on L_{av} (and on Δ^i_L) is explained by the asymmetry of the distribution of lengths, $N_L = f(L^i)$, of elementary links relative to L_{av}.

4. Conclusions

We have proposed a model for the calculation of an influence of the inhomogeneity of thicknesses of TiO_2 layers on the transport processes running in them. The simulation of the photoresponse of a layer with the Gauss statistics of the distribution over thicknesses has shown that the increase in the inhomogeneity of the distribution over thicknesses leads to a decrease of the "effective thickness" of a TiO_2 layer for the transport of electrons and, respectively, to an increase in the coefficient of diffusion. The simulation with the use of the real distributions of the thicknesses of TiO_2 layers ($\Delta_L \neq 0$), which were obtained with the help of a profilometer, has shown that the diffusion peak is in the limits of the interval $[t^0_{\text{peak}} - \Delta_t - t^0_{\text{peak}} + \Delta_t]$ in the case of the uniform thickness of a TiO_2 layer ($\Delta_L = 0$). This is explained by the asymmetry of the thickness distribution of a TiO_2 layer relative to the average thickness of a TiO_2 layer, L_{av}. The width of the thickness distribution depends on the stability of the process of application of a TiO_2 layer.

As a result of the simulation, we have obtained that the inhomogeneity of the thickness of a TiO_2 layer can significantly affect the total conductivity of the system. For the most nonuniform distribution over thicknesses, the relative deviation δt_{peak} was 22% (and that of the relevant coefficient of diffusion), which testifies the importance to account the inhomogeneity of the thickness of a transporting layer on the optimization of dye-based solar cells. Thus, the presence of the dispersion of thicknesses of TiO_2 layers leads to a variation in D_{eff} as compared with the case of a uniform thickness of a TiO_2 layer and causes a change of the diffusion length. Such a change determines, in its turn, the photocurrent of the system in the quasineutral region and influences both the short-circuit current and spectral characteristics of the system as a whole.

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МОДЕЛЮВАННЯ ВПЛИВУ НЕОДНОРІДНОСТІ ТОВЩИНИ НАНОКРИСТАЛІЧНИХ TiO_2-ШАРІВ НА ДИФУЗІЮ НОСІЇВ ЗАРЯДУ В СОНЯЧНОМУ ЕЛЕМЕНТІ НА ОСНОВІ ДИСПЕРСНОГО ГЕТЕРОПЕРЕХОДУ З БАРВНИКАМИ

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Резюме

Досліджено дифузійний транспорт в нанокристалічному TiO_2-шарі сонячного елемента на барвнику для різних значень неоднорідності товщини TiO_2-шару. Розроблено модель транспорту, що враховує вплив дисперсії товщини TiO_2-шару на сумарний відгук системи електроліт/TiO_2/FTO при імпульсному лазерному опроміненні. У цій моделі рух носіїв заряду крізь такий TiO_2-шар описується як рух через систему паралельних TiO_2-ланок різної довжини. Якщо врахувати дисперсію товщини TiO_2-шару, описавши її гаусівською функцією, розрахований в даній моделі коефіцієнт дифузії носіїв збільшується і положення дифузійного піка зсувається в бік коротших часів порівняно з бездисперсійним випадком. Обчислено дисперсію коефіцієнта дифузії для зразків різної товщини з розподілом по товщині, виміряним профілометром.